

**Isodisperse Telechelic Polymers and their Polyurethane Derivatives
Sample Preparation**

Final Technical Report

by

Ferenc Tüdös, Helga Tüdös and Tamara Földes-Bereznich

June, 1998

**United States Army
EUROPEAN RESEARCH OFFICE OF THE US ARMY
London, England**

Contract number: N 68171-95-C-9105

**TUDÓS '95 Ltd.
and
Eötvös Loránd University
Research Group of Macromolecular Chemistry
Hungarian Academy of Sciences**

**Felhö utca 18
H-1125 Budapest, Hungary
and
H-1518 Budapest 112, POB 32, Hungary**

19980707 111

Approved for public release; distribution unlimited

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188
<small>Provide reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of the collection of information, including suggestions for reducing this burden, to Department of Defense, Director for Information Operations and Reports, 1213 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4102, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>			
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	June 16, 1998	Final report Aug 1995-June 1998	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
Isodisperse Telechelic Polymers and their Polyurethane Derivatives: Sample Preparation		C: N68171-95-C-9105	
6. AUTHOR(S)			
Ferenc Tüdös, Helga Tüdös and Tamara Földes-Berezsich			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		8. PERFORMING ORGANIZATION REPORT NUMBER	
TUDÓS '95 Ltd. Research Group of Macromolecular Chemistry Felhő utca 18 of the Hungarian Academy of Sciences/ELTE H-1125 Budapest Pázmány P. sétány 2 Hungary H-1117 Budapest, Hungary			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
United States Army European Research Office Fiscal Office/Edison House; 223 Old Marylebone Road London, NW1 5TH United Kingdom			
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE	
<small>13. ABSTRACT (Maximum 200 words)</small> This report describes the preparation of six hydroxy-terminated polybutadiene (HTPBD) samples and their hydrogenated (polyethylene) derivatives (HTPE). The polybutadiene samples, with nominal average molecular weights M_n of 1000, 1500, 2000, 3000, 5000, and 10000, have been prepared using the so-called "isodisperse telechelic polymerization" method under non-isothermal conditions. The HTPBD samples produced were characterized by gel permeation chromatography, FT-IR and $^1\text{H-NMR}$ and showed a narrow polydispersity approaching the theoretical limit. From the HTPBD samples isodisperse HTPE samples were prepared by hydrogenation under heterogeneous conditions, using a freshly prepared 30% palladium/charcoal catalyst. Between July 1995 and May 1997, 100-g batches of the twelve samples thus prepared were sent to the US army research laboratory for further experiments.			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
Isodisperse telechelic polymers, hydroxy-terminated polybutadienes, hydroxy-terminated polyethylenes, non-isothermal polymerization		52	
16. PRICE CODE			
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
<small>NSN 7540-01-280-5500</small>			

Abstract

This report describes the preparation of six hydroxy-terminated polybutadiene (HTPBD) samples and their hydrogenated (polyethylene) derivatives (HTPE). The polybutadiene samples, with nominal average molecular weights M_n of 1000, 1500, 2000, 3000, 5000, and 10000, have been prepared using the so-called "isodisperse telechelic polymerization" method under non-isothermal conditions. The HTPBD samples produced were characterized by gel permeation chromatography, FT-IR and $^1\text{H-NMR}$ and showed a narrow polydispersity approaching the theoretical limit. From the HTPBD samples isodisperse HTPE samples were prepared by hydrogenation under heterogeneous conditions, using a freshly prepared 30% palladium/charcoal catalyst. Between July 1995 and May 1997, 100-g batches of the twelve samples thus prepared were sent to the US army research laboratory for further experiments.

Keywords: isodisperse telechelic polymerization, hydroxy-terminated polybutadienes, hydroxy-terminated polyethylenes, non-isothermal polymerization, hydrogenation

Table of Contents

Title Page (Form 298)	1
Abstract	2
Table of Contents	3
Introduction	4
Experimental	5
Preparation of HTPBD samples	6
Preparation of HTPE samples	9
Conclusions	11
References	12
Annex 1: Characterization of HTPBD samples	
Annex 2: Characterization of HTPE samples	

Introduction

In the past decade there has been a great interest in hydroxy telechelic polymers with designed low molecular weights and narrow polydispersity. There may be several applications for this type of polymers:

- ◆ Incorporation into a polymeric matrix to alter its physical properties such as viscosity.
- ◆ Chemical modification of the reactive sites: the hydroxy end groups can be converted into acrylic, acid or acid chloride groups.
- ◆ Crosslinking with multifunctional reagents to obtain macromolecular networks.

Free-radical polymerization is probably the most cost-effective for preparing such polymers with functional groups in the α,ω positions [2, 3]. In that case the functionality is determined by the nature of the initiating radicals. However, controlling polydispersity has often been a problem in free-radical polymerizations. This is mainly related to changing conditions during the polymerization reaction: decreasing concentrations of initiator and monomer, and increasing viscosity. At the Research Group of Macromolecular Chemistry of the Hungarian Academy of Sciences, a method was developed to counteract these effects and produce polymers with minimal polydispersity P_w/P_n [4]. In theory, in the case of recombination, the polydispersity P.D. equals 1.5 and the functionality F of the polymer equals 2.

The US Army Research Laboratory is interested in obtaining elastomers with optimal physico-chemical properties. Isodisperse telechelic polymers such as HTPBD or HTPE could constitute such materials according to the theory of elasticity. This report describes the synthesis and chromatographic/spectroscopic characterization of six HTPBD samples with nominal average molecular weights M_n of 1000, 1500, 2000, 3000, 5000, and 10000. The optimization of the reaction conditions and the development of the corresponding temperature programs has been described in detail in our previous report "Isodisperse Telechelic Polymers and their Polyurethane Derivatives" (contract # N68171-95-C-9068) [1]. Six HTPE samples were then prepared from their HTPBD precursors through hydrogenation using a palladium/charcoal catalyst. The twelve samples were sent to the US Army Research Laboratory in 100-g amounts for further characterization.

Experimental

Chemicals

4,4'-azo bis-4-cyano-*n*-pentanol (ACP) synthesized in our own laboratory from 5-hydroxy-2-pentanone (Fluka); molecular weight: 252; melting point: 81-83 °C or 94-96°C (two isomers). Hydrogen peroxide, 50% solution by weight, from Peroxid Chemie GmbH, Germany. 1,3-butadiene, purity > 99% from Matheson.

Polymerization

The polymerization reactions were carried out in an acid-proof autoclave from Parr (net volume 900 ml; maximum pressure 190 bar). The reactor can be stirred mechanically, electrical heating and cooling with circulating water can be applied from the outside. After addition of all solvents and dissolution of the initiator the reactor is flushed with pure nitrogen and evacuated several times. Then the monomer (preheated to 30°C) is added in liquid form from a buffer vessel and the polymerization reaction is started according to a specific temperature program.

Purification

After the polymerization reaction the pressure is released and the unreacted monomer is condensed and recovered. The recombination product from initiator and hydrogen peroxide is removed by washing with distilled water in a separation funnel. The remaining peroxide is reduced to below 1 ppm level by passing through a zeolite column activated with cobalt ion. The solvents are removed in a film evaporator by nitrogen heated to 140°C [1].

Hydrogenation

3 g of freshly prepared 30% Pd/C catalyst and 30 ml of *n*-hexane was placed in a Parr hydrogenation apparatus. After repeated flushing/evacuation with nitrogen and then with hydrogen the catalyst was hydrogenated for 20 minutes at 60°C and 4 bar. Then 10 g of the HTPBD sample was added in 370 ml of *n*-hexane and was hydrogenated at 60°C and 4 bar during 1 hour. After filtration over a glass filter the catalyst was washed and the solvent was evaporated under vacuum. Eleven batches were prepared and combined to yield the amount required. Heating to 100°C under reduced pressure served to remove the last traces of solvent. See also ref. [5].

Instrumental Analysis

Proton NMR spectra were recorded using a Varian 400 instrument. Fourier transform infrared spectra (FT-IR) were recorded using a Bomem MB-100 spectrophotometer. The molecular weight distribution was determined by means of gel permeation chromatography (GPC) using a setup from Waters: pump model 510, injector model U6K and a set of four columns packed with crosslinked polystyrene gel (“ultrastyragel”) of particle size less than 10 microns and pore sizes of 10 µm, 1 µm, 100 nm and 50 nm.

The functionality of the polymers was calculated from the hydroxy-endgroup concentration and the molecular weight of the polymers, as described in our previous report [1]. The apolar solvent used (cyclohexane) precludes any interference from the ACP initiator recombination product, as it is insoluble in this solvent.

Preparation of HTPBD Samples

Polybutadiene samples were synthesized with nominal average molecular weights M_n of 1000, 1500, 2000, 3000, 5000, and 10000. The polymerization conditions applied are listed in Table 1. The details of the non-isothermal temperature programs have been described earlier [1].

Table 1: Polymerization conditions and reagents used.

Samples	Monomer mol/l	Solvent (ml)		Initiator (mol/l)		Polym. time (min)	Temp. °C
		sec. butanol	dioxane	ACP	H_2O_2		
HTPBD-1000	6.0	200	200	0.145	-	175	73-96
HTPBD-1500	6.0	200	200	0.145	-	500	65-96
HTPBD-2000	6.0	400	-	2.14E-02	0.63	180	80-96
HTPBD-3000	6.0	400	-	2.14E-02	0.53	360	75-96
HTPBD-5000	6.0	400	-	5.73E-03	0.18	480	70-96
HTPBD-10000	6.0	200	200	8.00E-04	6.15E-03	720	70-96

The functionality of the HTPBD samples was determined and was found to be close to the theoretical value of 2 for all samples (see Table 2). The conversion rates of the polymerization reactions varied between 20 and 40% for most samples, but was only 10% for the HTPBD-10000 sample (see Table 2). The experimentally determined average molecular weights and polydispersity data (as measured by GPC) are also listed in Table 2 and visualized in Figure 1.

Table 2: Functionality, conversion rates and polydispersity of HTPBD samples

Samples	Functionality	Conversion %	GPC results	
			M_n	M_w/M_n
HTPBD-1000	1.62	30.0	1245	1.34
HTPBD-1500	2.10	33.0	1552	1.34
HTPBD-2000	1.90	20.0	1870	1.62
HTPBD-3000	2.44	40.0	3250	1.98
HTPBD-5000	1.98	25.0	5230	1.72
HTPBD-10000	1.97	10.0	10800	1.95

As shown in Table 2, the molecular weight distribution of the samples HTPBD-1000 and HTPBD-1500 is very low, even below the theoretical value of 1.5. These low polydispersities can be expected to have a very positive effect on the elastic properties of the resulting polyurethane materials according to the elasticity theory.

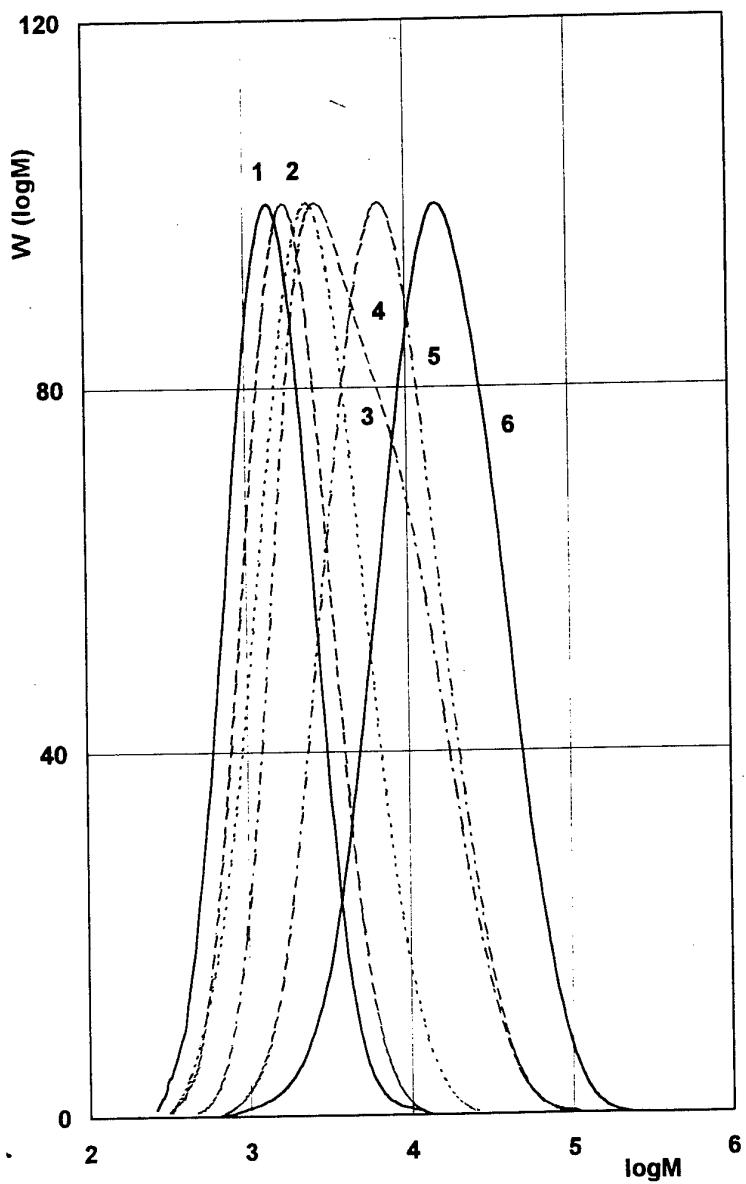


Figure 1: Molecular weight distribution of the HTPBD samples, as determined by GPC.
1= HTPBD-1000; 2= HTPBD-1500; 3= HTPBD-2000; 4= HTPBD-3000; 5= HTPBD-5000; 6= HTPBD-10000.

The microstructure of the HTPBD samples was investigated using FT-IR and ¹H-NMR spectroscopy; the spectra can be found in Annex 1. The FT-IR spectra show only a few differences between the samples. Obviously the broad OH-stretch absorption at 3200-3600 cm⁻¹ (hydroxy endgroups) is relatively strong for the short oligomers and practically invisible for the HTPBD-5000 and HTPBD-10000 samples. For the same reason the cyanide stretch vibration (initiator fragments) is most strongly observed in the spectra of the shortest oligomers.

During the course of the polymerization three different configurations can be formed: 1,4-trans, 1,2- and 1,4-cis linkages. The distribution of these linkages was determined based on the ratios of a number of out-of-plane IR vibrational absorptions, as described in our previous report [1]. The ratio between the number of 1,2-linkages and 1,4-linkages was also determined by proton NMR spectroscopy; the two configurations can be distinguished based on the unsaturated proton intensities at 4.9-5.0 and 5.2-5.4 ppm, respectively [1]. In general, the results of the two techniques agree quite well, although in general the percentage of 1,2-linkages appears to be a little higher according to the NMR results in comparison to the FT-IR results (see Table 3). In general, the ratio of 1,2-linkages vs. 1,4-linkages is about 1 to 5 in all samples, irrespective of the average chain length.

Table 3: Microstructure of HTPBD samples based on FT-IR and NMR results (%).

Samples	FT-IR			proton NMR	
	1,2 link	1,4 link <i>cis</i>	1,4 link <i>trans</i>	1,2 link	1,4 link
HTPBD-1000	11	54	35	15	85
HTPBD-1500	11	58	31	15	85
HTPBD-2000	13	54	33	17	83
HTPBD-3000	13	53	34	18	82
HTPBD-5000	13	54	33	17	83
HTPBD-10000	13	59	28	14	86

Preparation of HTPE Samples

Before the hydrogenation, new batches of HTPBD were prepared, using approximately the same conditions as those employed for the first set of HTPBD samples. The resulting products were analyzed by GPC, FT-IR and proton NMR, and the OH-functionality was also determined. Again the resulting polydispersities were quite narrow ($1.5 < 2$) and again the polydispersity was smallest in the case of samples HTPBD-1000 and HTPBD-1500 (see Table 4). Using the same method as described above, FT-IR and proton NMR spectroscopy was employed to determine the distribution of 1,2-linked *vs.* 1,4-*trans* linked *vs.* 1,4-*cis* linked configurations of these precursor HTPBD polymers and the results were very similar to those obtained with the first batch (compare Table 3 and Table 5). Most of these structural investigations were carried out on the precursor HTPBD polymer rather than on the HTPE endproduct, as the solid nature of the polyethylene samples and their insolubility in most solvents would preclude such measurements of the endproduct, unless extremely powerful solvents such as trichlorobenzene and very high temperatures were used. Under the mild hydrogenation conditions applied in our laboratory the structural characteristics of the HTPBD chains (length, configuration of linkages) will remain unchanged and will therefore also describe the HTPE polymer samples. Of course the molecular weight of the oligomers will increase by 3.7 % due to the addition of two hydrogens per butadiene group.

Table 4: Functionality and polydispersity of precursor HTPBD samples used for the preparation of hydroxy-terminated polyethylene.

Samples	Functionality	GPC results	
		M_n	M_w/M_n
HTPBD-1000	1.98	1211	1.54
HTPBD-1500	2.03	1666	1.53
HTPBD-2000	2.01	2136	1.79
HTPBD-3000	2.05	3059	1.78
HTPBD-5000	1.97	5403	1.81
HTPBD-10000	1.99	10270	1.79

Table 5: Microstructure of precursor HTPBD samples based on FT-IR and NMR (%)

Samples	FT-IR			proton NMR	
	1,2 link	1,4 link <i>cis</i>	1,4 link <i>trans</i>	1,2 link	1,4 link
HTPBD-1000	11	54	35	17	83
HTPBD-1500	12	55	33	17	83
HTPBD-2000	11	55	34	17	83
HTPBD-3000	12	55	33	18	82
HTPBD-5000	12	54	34	17.5	82.5
HTPBD-10000	12	58	30	17.5	82.5

Hydrogenation of unsaturated polymers can, in principle, be accomplished in several ways. Several hydrogenation procedures were tested on small batches of polybutadiene polymer HTPBD-3000. Proton NMR was employed to determine the completeness of the reduction. Homogeneous catalysis with chloro-tris(triphenyl-phosphine)rhodium(I) was tested, and although the resulting product showed an almost complete reduction, the practical difficulties of removing catalyst traces from the product constituted a major drawback. Reductions under heterogeneous conditions with hydrazine hydrate as reducing agent and Raney-nickel or 10% Pd/C or PtO₂ as catalyst also failed. The best results were obtained using hydrogenated Pd/C in n-hexane. See the Experimental section and ref. [5] for further details on the hydrogenation experiments.

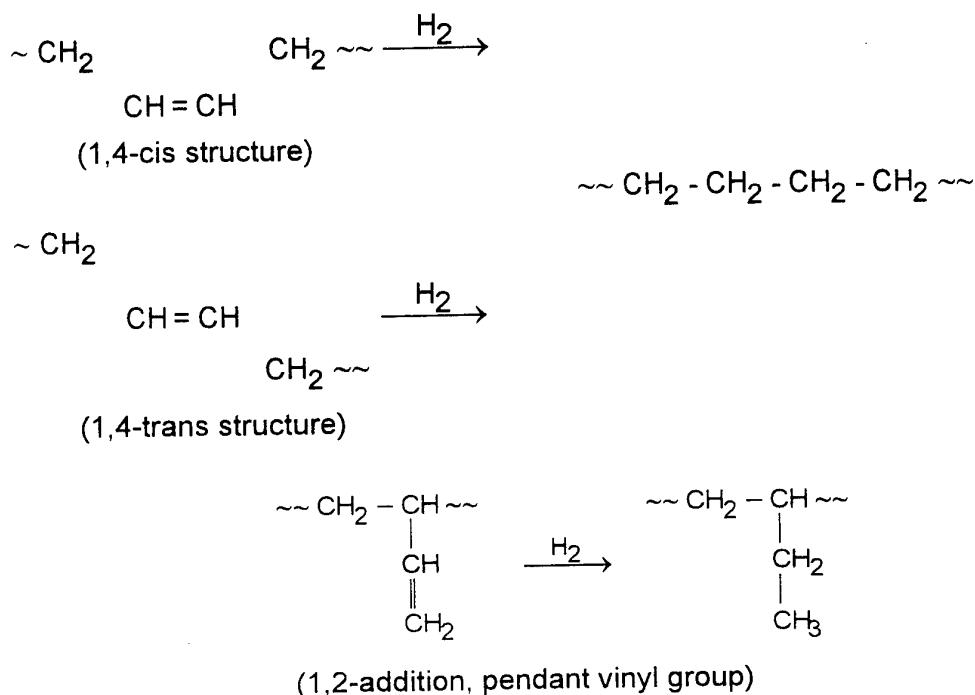


Fig. 2: Hydrogenation of 1,4-cis, 1,4-trans and 1,2 linked butadiene groups.

Figure 2 shows the structures resulting from hydrogenation of 1,4-linked and 1,2 linked polybutadienes. Given the mild hydrogenation conditions no structural changes or chain fission will occur. The hydrogenation of the above mentioned HTPBD samples led to the following products: HTP-1000, HTP-1500, HTP-2000, HTP-3000, HTP-5000, HTP-10000. These were analyzed by means of proton NMR before dispatching them to the US Army Research Laboratory (see Annex 2).

Conclusions

In a previous stage of this project the optimal conditions for non-isothermal radical polymerization were theoretically derived and the corresponding temperature programs were developed. This report describes the successful application of this approach to the synthesis of bifunctional polybutadiene polymers with a uniform chain length. Indeed for all samples a narrow polydispersity $M_w/M_n < 2$ was observed with gel permeation chromatography. The average molecular weights were usually well within 10-20 % of the target values.

From a second series of HTPBD samples showing similarly low polydispersity the corresponding saturated polyethylene derivatives were prepared by hydrogenation under heterogeneous catalytic conditions (Pd/C). One of the major advantages of this method is the easy separation and recovery of the catalyst.

This work has shown the potential of temperature-programmed radical polymerization for the production of polymers with uniform chain lengths. Application of these principles to the production of isodisperse copolymers has also been successful [6]. Such materials could ultimately be of great value for the production of cross-linked rubbers with excellent elastic properties.

Table 6: HTPBD and HTPE samples shipped to the US Army Research Laboratory

Samples	Shipping date	Mn
HTPBD-1000	Jan 25, 1996	1245
HTPBD-1500	Jan 25, 1996	1552
HTPBD-2000	Oct 13, 1995	1870
HTPBD-3000	July 6, 1995	3250
HTPBD-5000	Oct 13, 1995	5230
HTPBD-10000	Jan 25, 1996	10800
HTPE-1000	May 28, 1997	1256
HTPE-1500	May 28, 1997	1728
HTPE-2000	Feb 11, 1997	2215
HTPE-3000	March 7, 1997	3172
HTPE-5000	April 9, 1997	5603
HTPE-10000	April 9, 1997	10650

References

- 1 F. Tüdös and T. Földes-Berzsнич. Isodisperse Telechelic Polymers and their Polyurethane Derivatives. Final report US Army contract # N68171-95-C-9086 (1996).
- 2 J.C. Brosse, M. Bonnier, and G. Legeay. *Macromol. Chem.* **183**, 313 (1982).
- 3 C.A. Uraneck, H.L. Hsieh, and O.G. Buck. *J. Polym. Sci.* **46**, 535 (1960).
- 4 Földes Pné, Gy. Mikétáné Fenyvesi, A. Nagy, T. Pernecker, Á Rehák, D. Szalay, and F. Tüdös. Hungarian Pat: 201.101 (1986.11.14.) 4693/86; 1990.09.28; USA Pat. 5,126,415.
- 5 F. Tüdös. Isodisperse Telechelic Polymers and their Polyurethane Derivatives. US Army contract # N68171-97-C-9002. 4th interim report (1997).
- 6 F. Tüdös. Isodisperse Telechelic Polymers and their Polyurethane Derivatives. US Army contract # N68171-97-C-9002. 5th interim report (1998).

ANNEX 1

CHARACTERIZATION OF HTPBD SAMPLES

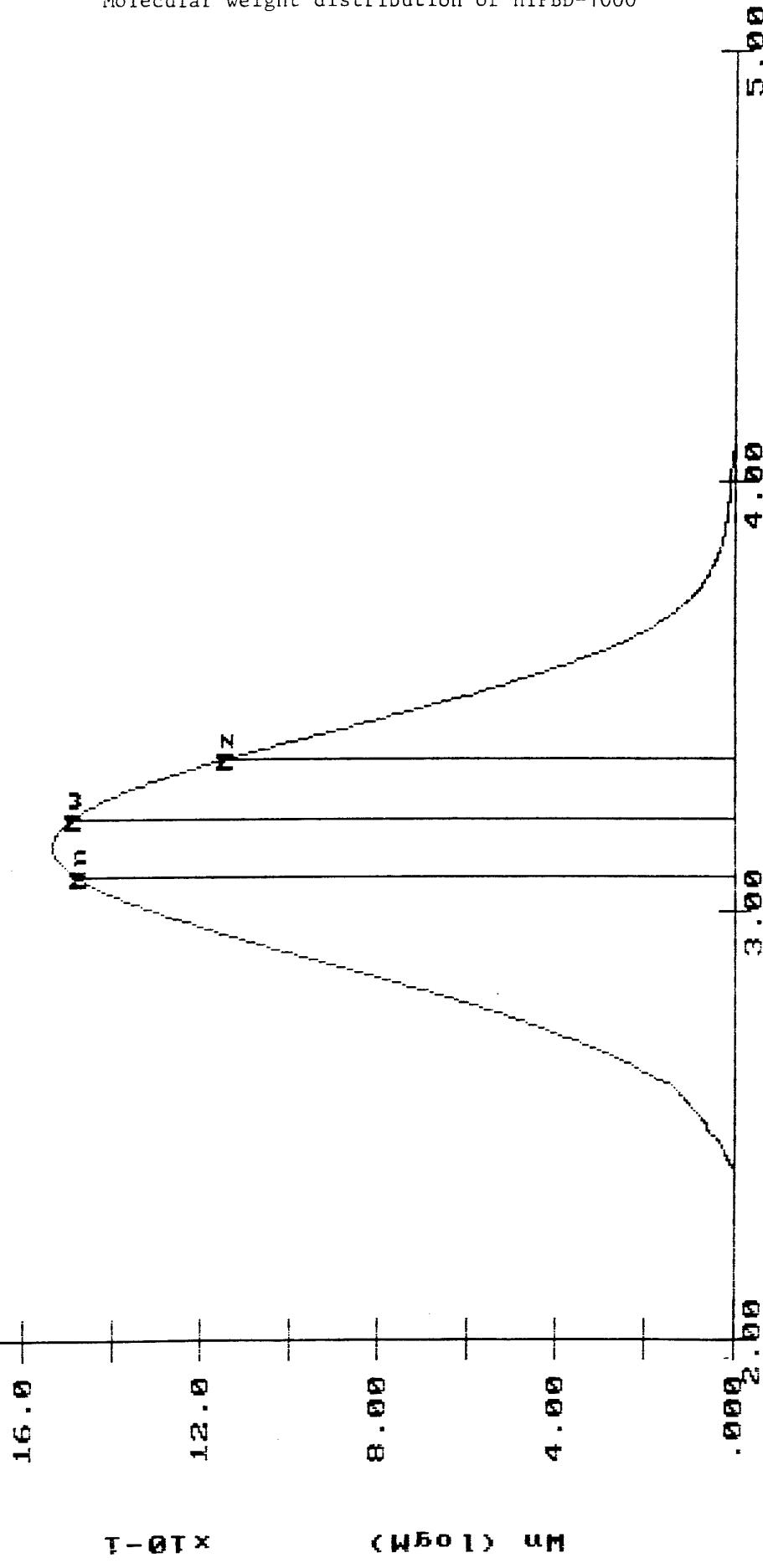
- ◆ Molecular weight distribution of HTPBD-1000
- ◆ Molecular weight distribution of HTPBD-1500
- ◆ Molecular weight distribution of HTPBD-2000
- ◆ Molecular weight distribution of HTPBD-3000
- ◆ Molecular weight distribution of HTPBD-5000
- ◆ Molecular weight distribution of HTPBD-10000
- ◆ FT-IR spectra of HTPBD-2000, HTPBD-3000, and HTPBD-5000
- ◆ FT-IR spectra of HTPBD-10000, HTPBD-1500, and HTPBD-1000
- ◆ Proton-NMR spectrum of HTPBD-1000
- ◆ Proton-NMR spectrum of HTPBD-1500
- ◆ Proton-NMR spectrum of HTPBD-2000
- ◆ Proton-NMR spectrum of HTPBD-3000
- ◆ Proton-NMR spectrum of HTPBD-5000
- ◆ Proton-NMR spectrum of HTPBD-10000

DISCOTEK CORP. UCAL 4.05
FILE NAME: 1372aa RUN ID: 95/325 Polibut. 137/2
Mn = 1.25E3
Mw = 1.67E3
Mz = 2.25E3

Molecular weight distribution of HTPBD-1000

MOLECULAR WEIGHT DISTRIBUTION

HTPBD-1000



LOG M

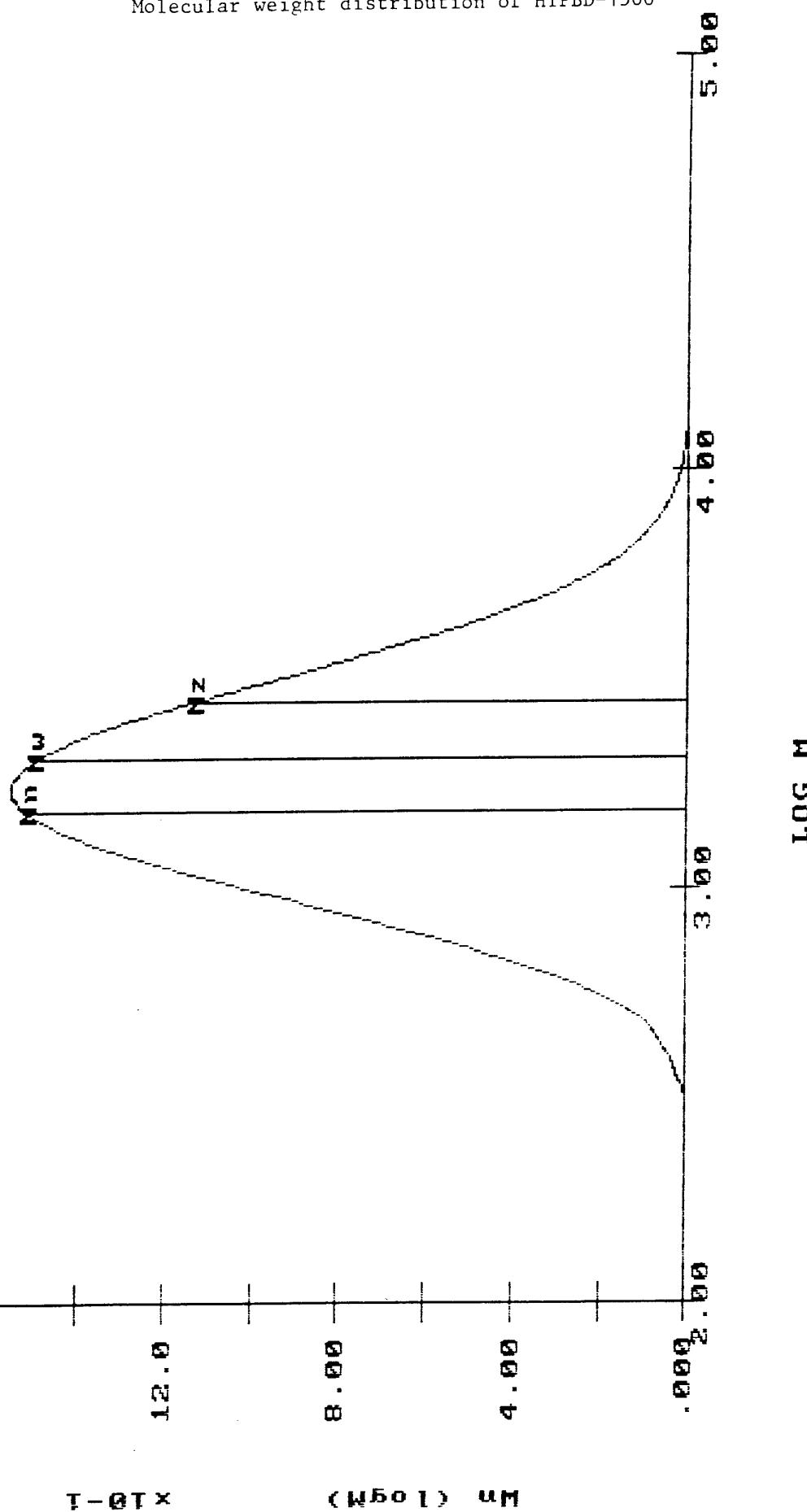
WISCOTEK CORP. UCAL 4.05
FILE NAME: 13044aaa RUN ID: 95/303 Pollut. 130/44a
Mn = 1.53E3

Mw = 2.07E3

Mz = 2.84E3

MOLECULAR WEIGHT DISTRIBUTION
HTPBD-1500

Molecular weight distribution of HTPBD-1500



UISCOTEK CORP. UCAL 4.05

ENDED: 06/2

ENDED : 06/22/95 10:44

15.0 \pm Mn = 1.88E3

$M_u = 3.03E3$

$$M_2 = 4.96 \times 10^3$$

8E3

3E3

GE3

MOLECULAR WEIGHT DISTRIBUTION

HITPBD-2000

12.9 —

T-91X

(ИБС 1) и М

A line graph with a vertical y-axis and a horizontal x-axis. The y-axis has major tick marks at 2.00, 3.00, 4.00, 5.00, and 6.00. The x-axis is labeled '100' at the far right. A single data series is plotted as a solid line, starting at (0, 6.00) and ending at (100, 2.00). The line is concave down, indicating a decreasing rate of change.

VISCOTEK CORP. UCAL 4.05
FILENAME: pb120d RUN ID: 95/146 Polibut.

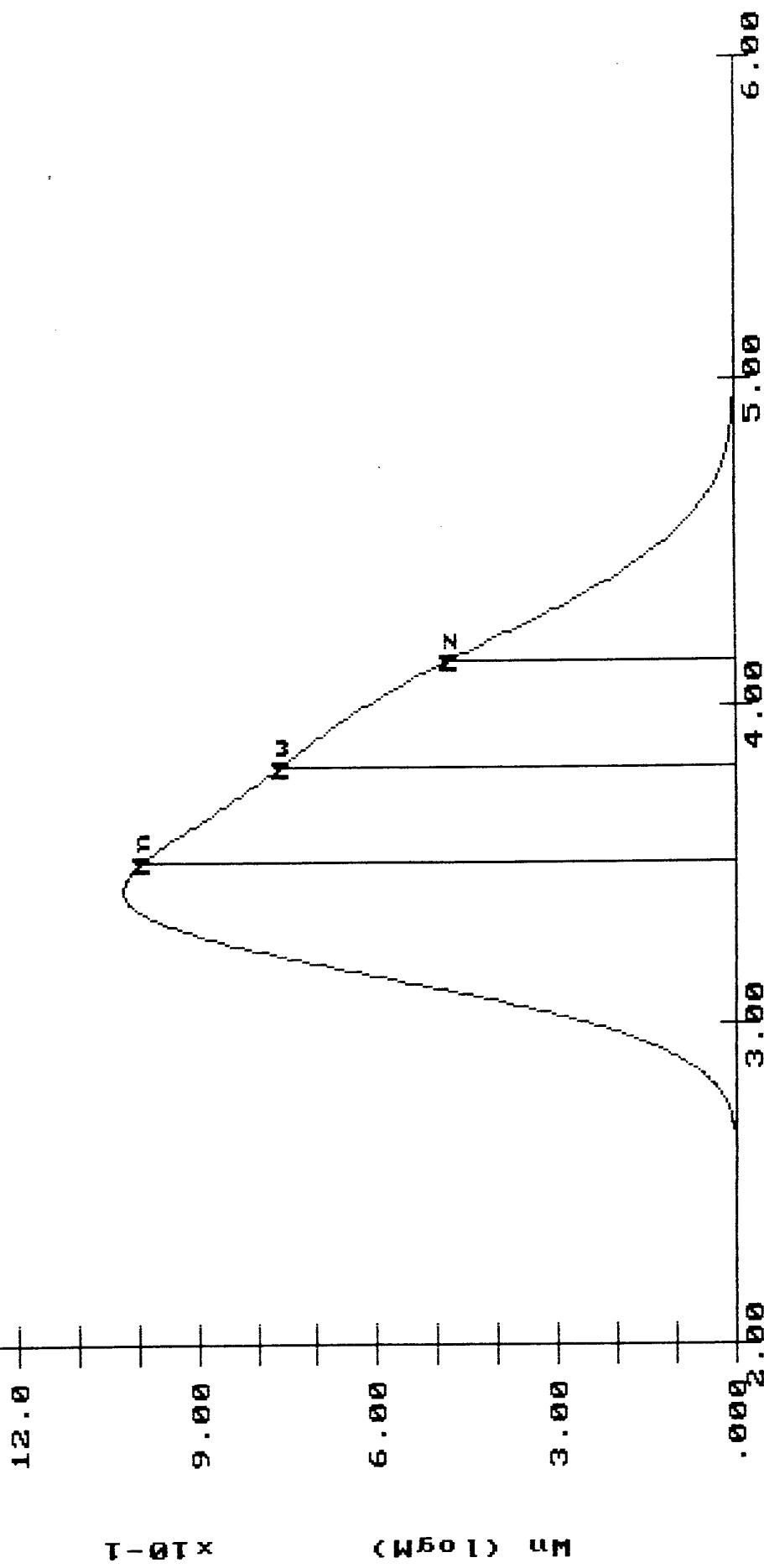
$M_n = 3.24 \times 10^3$

$M_w = 6.45 \times 10^3$

$M_z = 1.38 \times 10^4$

MOLECULAR WEIGHT DISTRIBUTION

HTPBD-3000

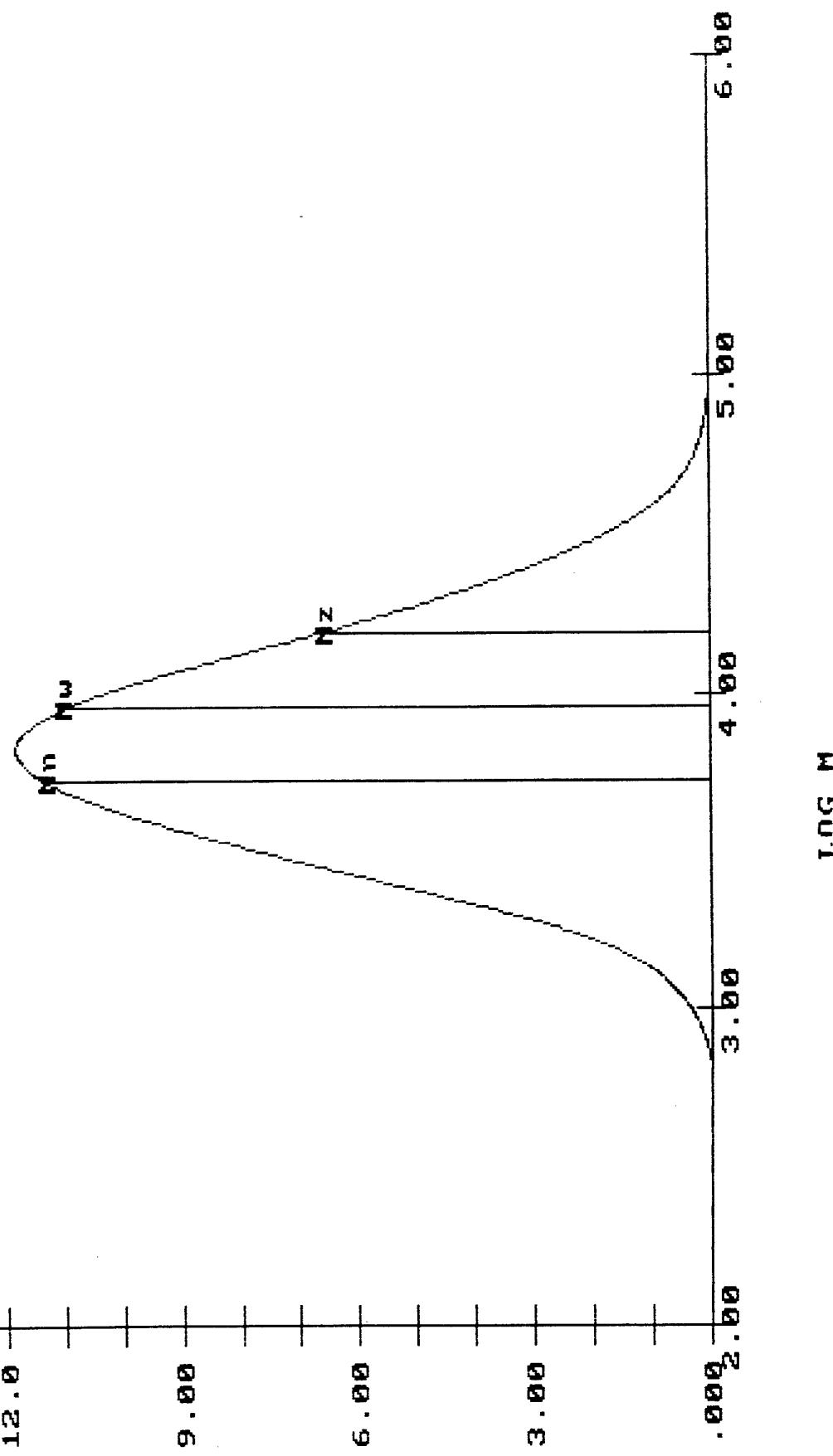


VISCOTEK CORP. UCAL 4.05
FILENAME: 5Ka RUN ID: 95/272 Polibut. 5Ka

ENDED: 10/05/95 15:02
Molecular Weight Distribution

$M_n = 5.26 \times 10^3$
 $M_w = 9.02 \times 10^3$
 $M_z = 1.57 \times 10^4$

T-GTX (M501) 5



ENDU : 01/03/96 14:06

UML : 0.0

FILENAME: x6a
RUN ID: 96/1 polybut. x-6
Mn = 1.08E4
Mw = 2.10E4
Mz = 3.78E4

MOLECULAR WEIGHT DISTRIBUTION
HTPBD-10000

Molecular weight distribution of HTPBD-10000

T-0Tx

MW (10⁴) g

12.0

9.00

6.00

3.00

0.00

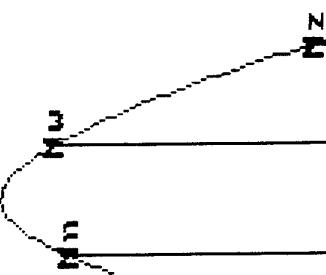
6.00

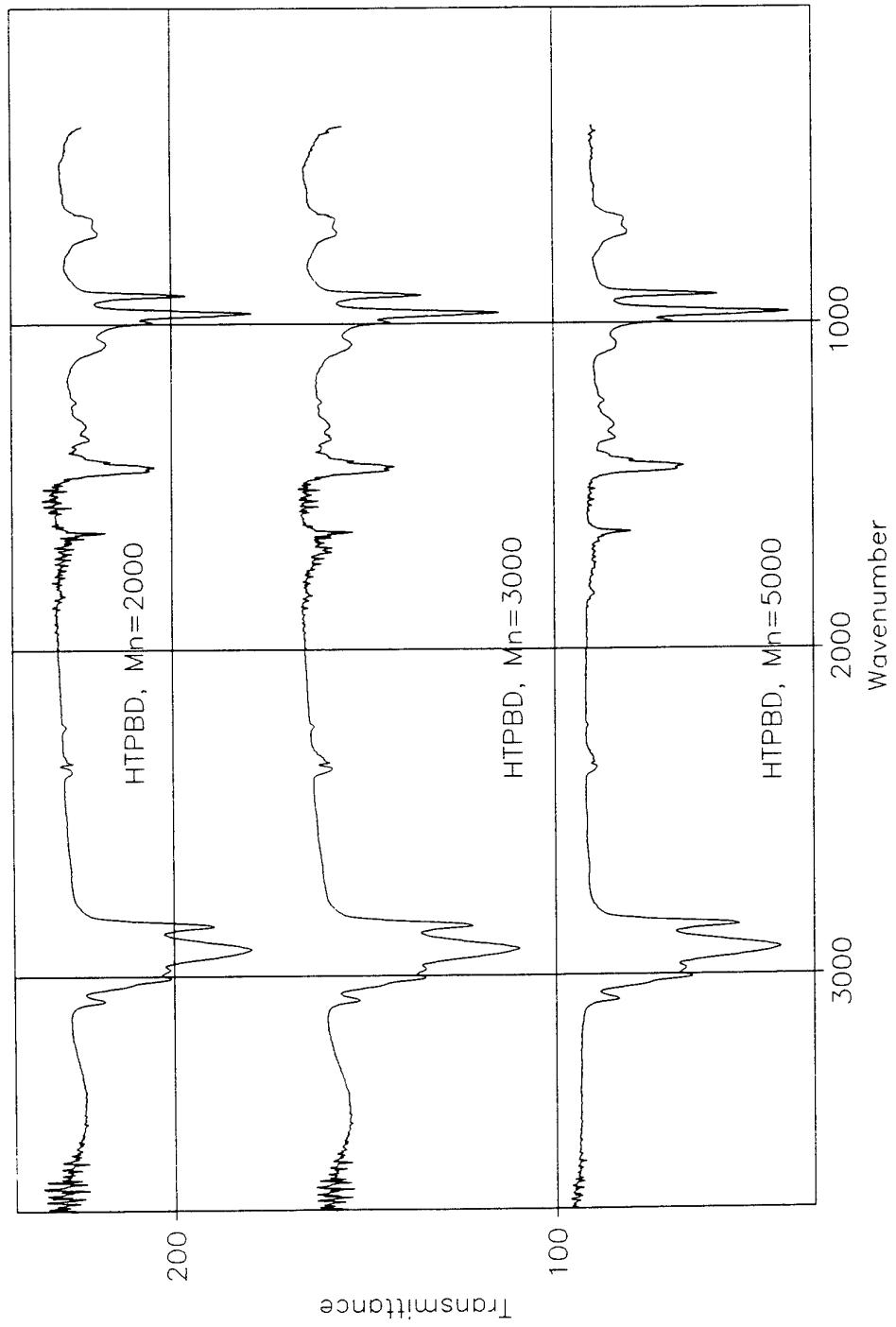
5.00

4.00

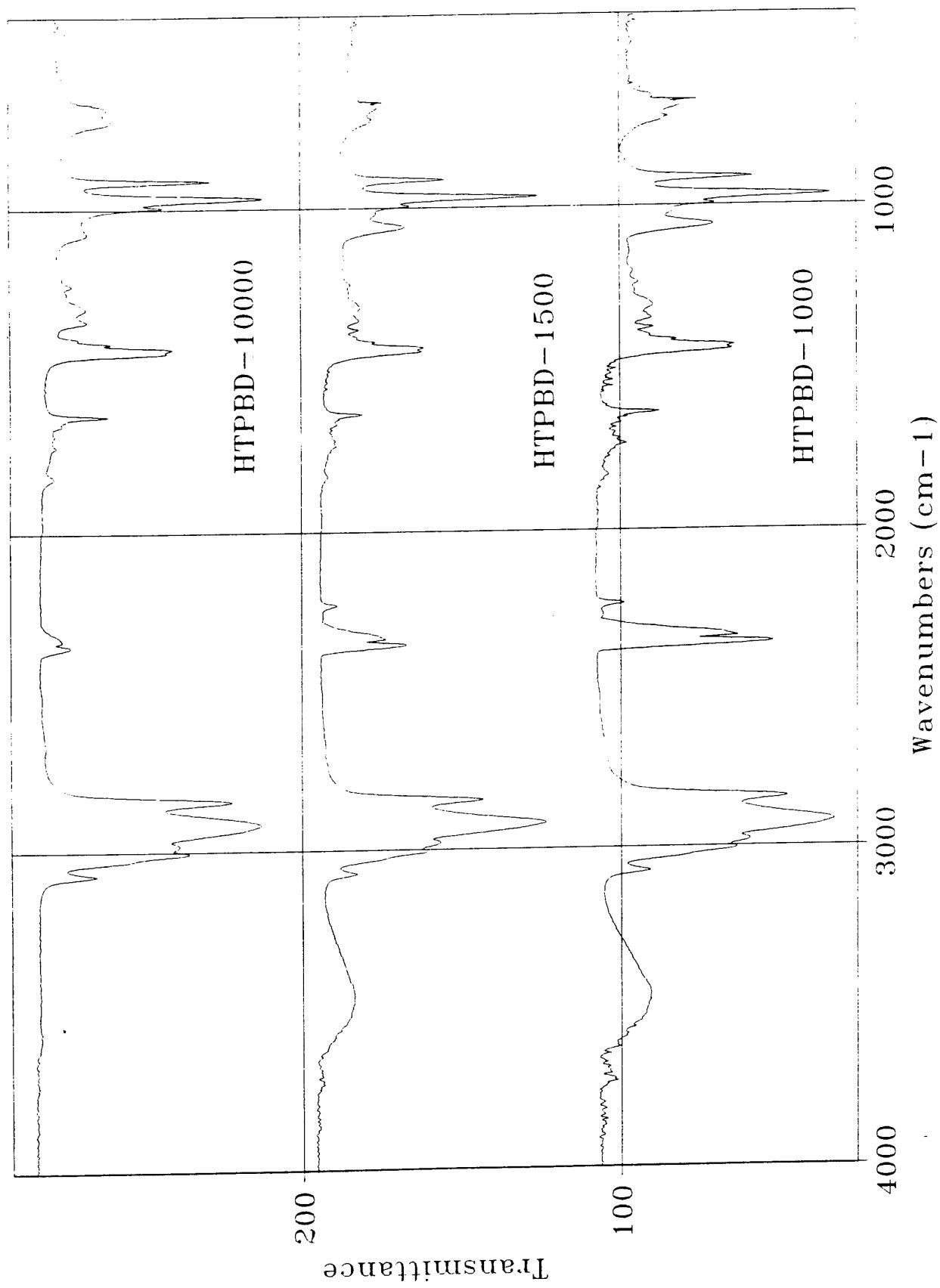
3.00

LOG M





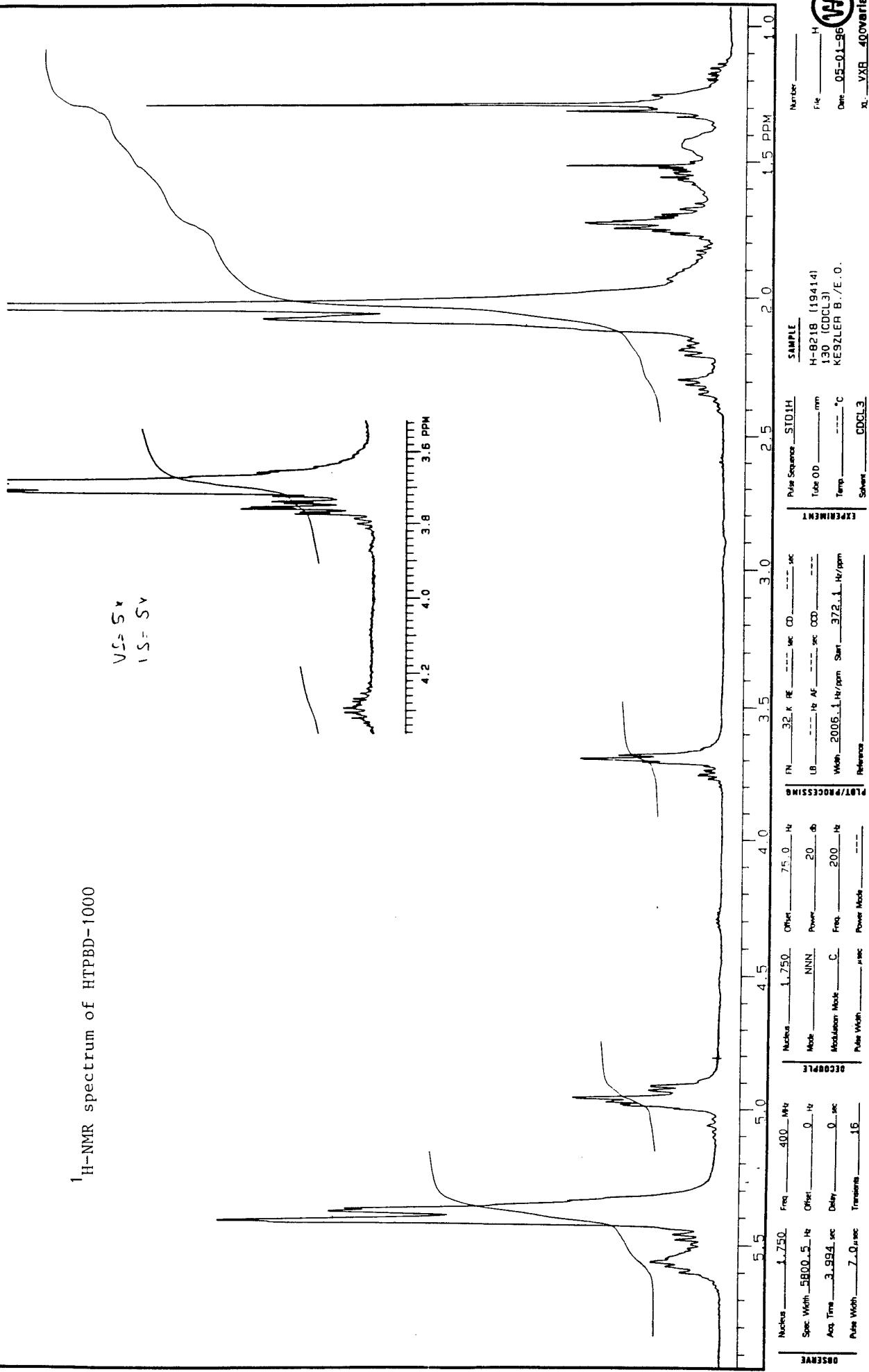
FT-IR spectra of polybutadiene diol samples.



FT-IR Spectra of HTPBD samples.

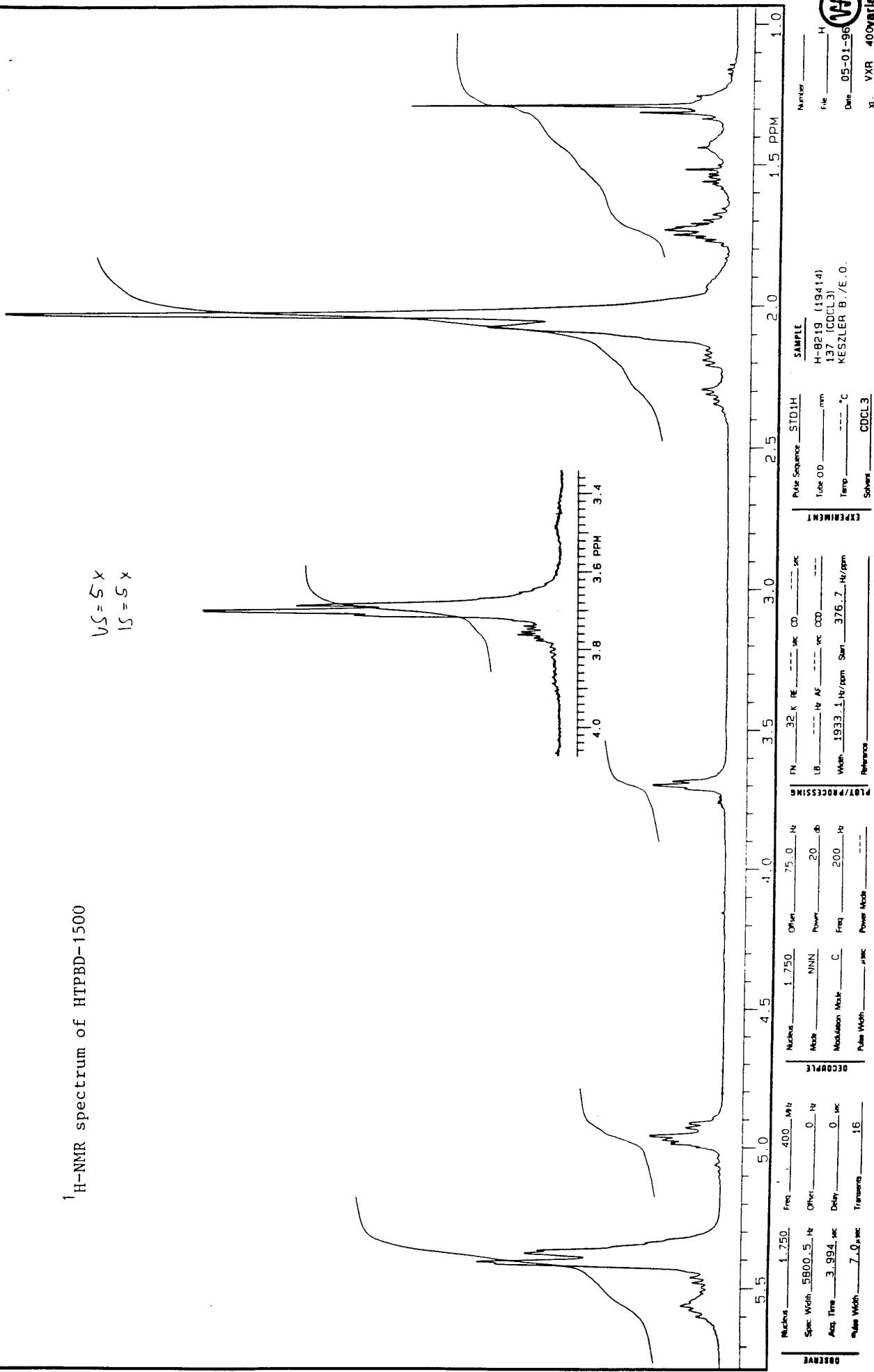


51

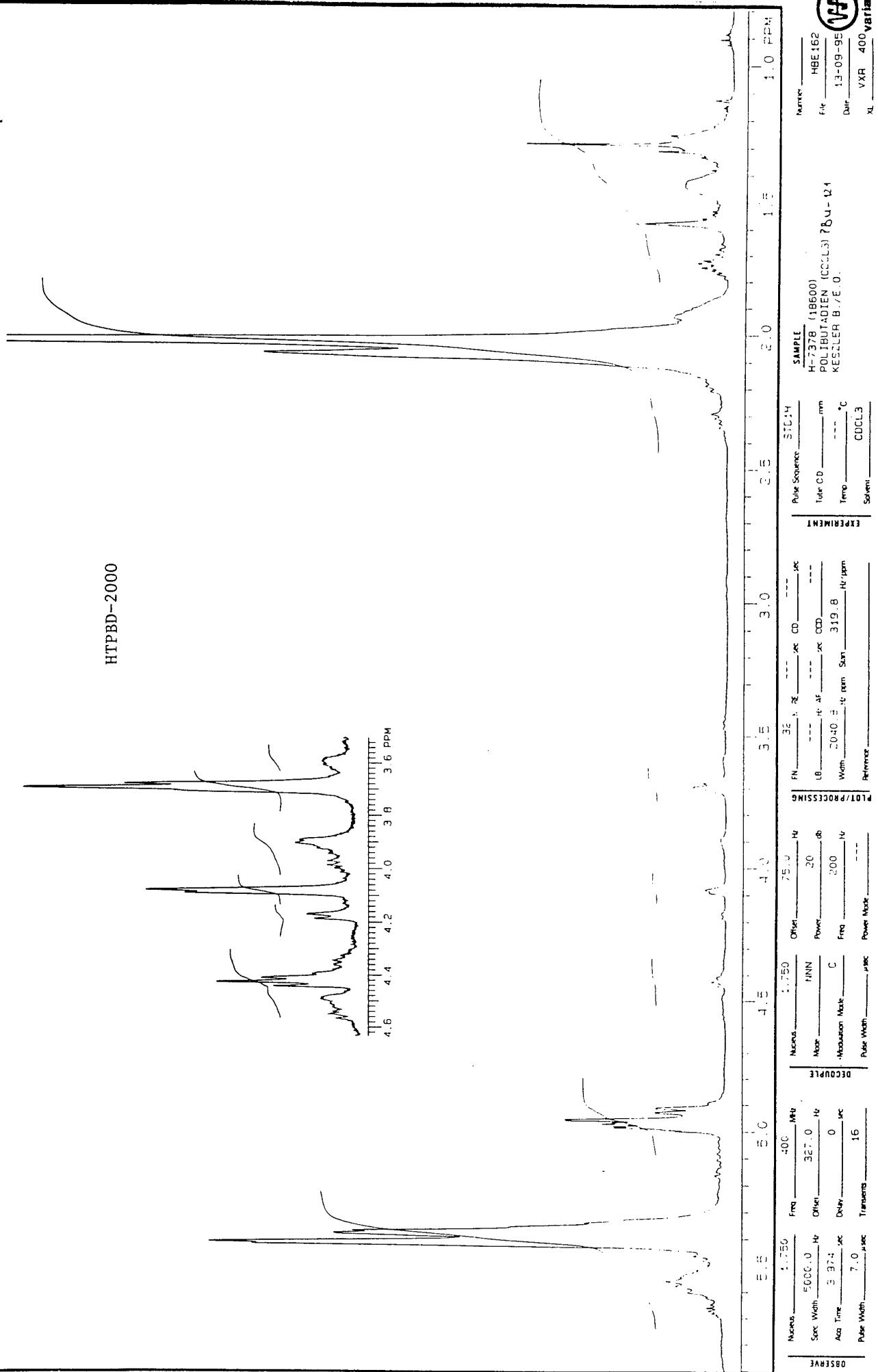


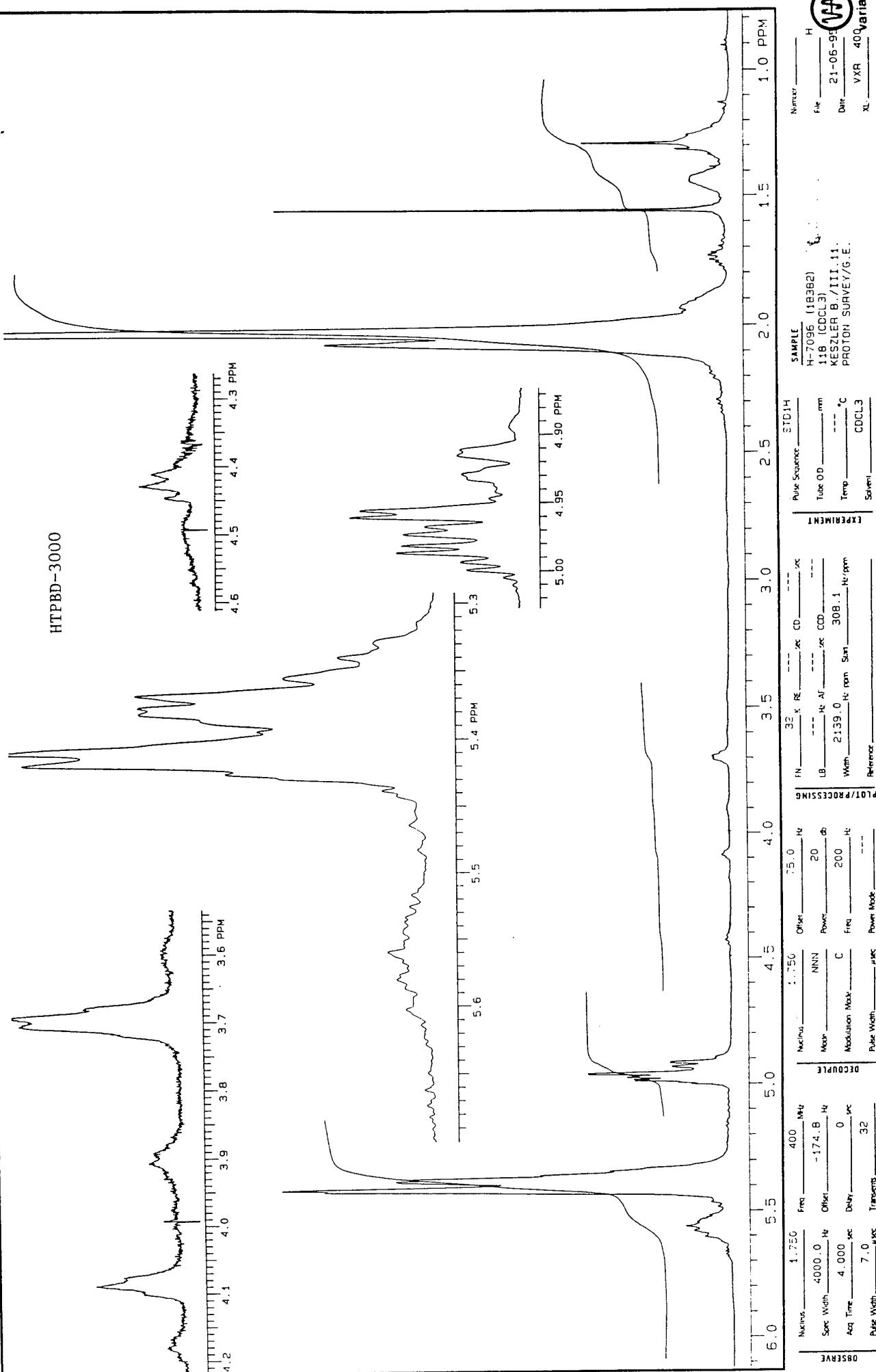
¹H-NMR spectrum of HTPBD-1500

$$x = y$$

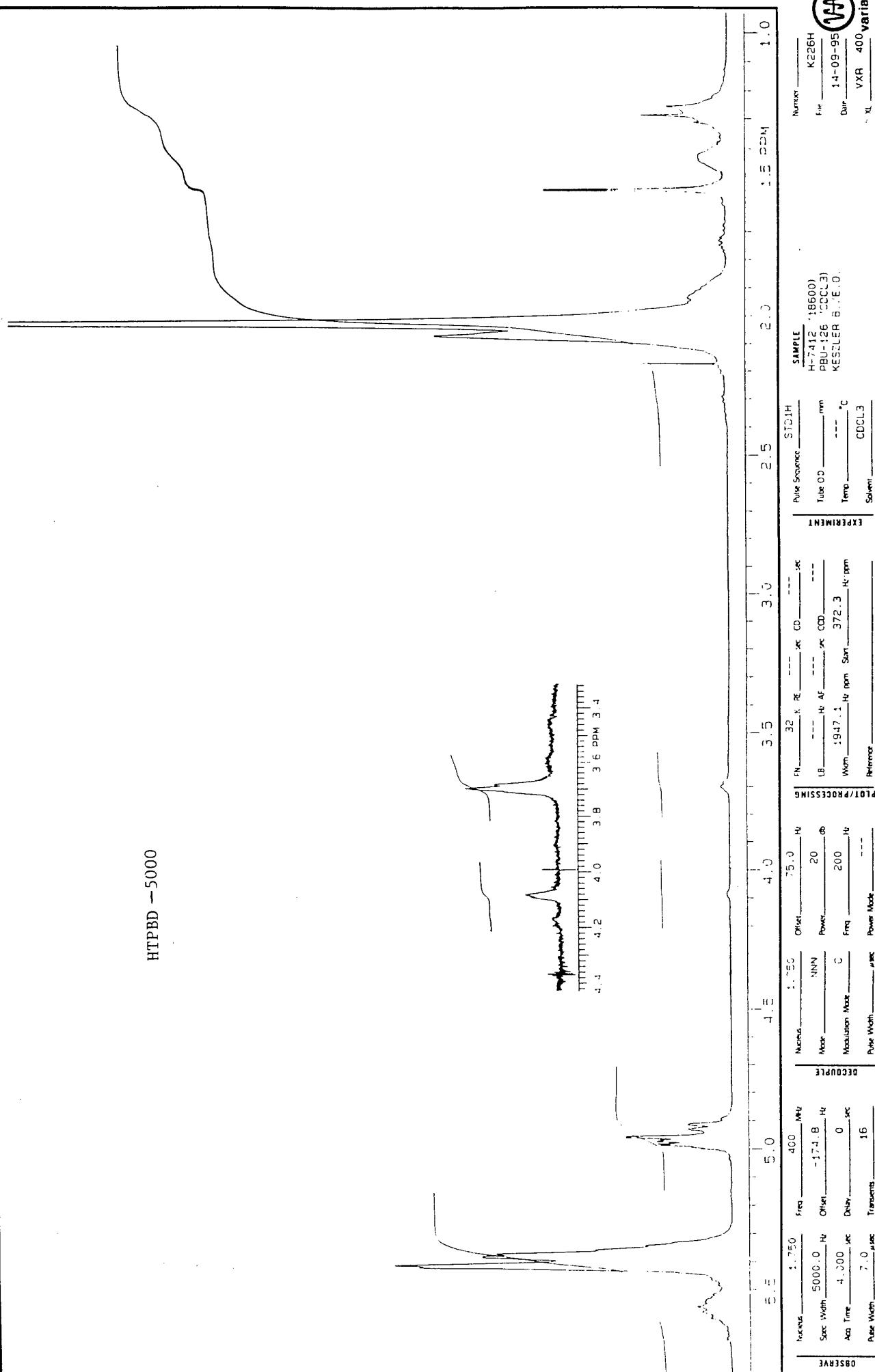


HTPB-D-2000

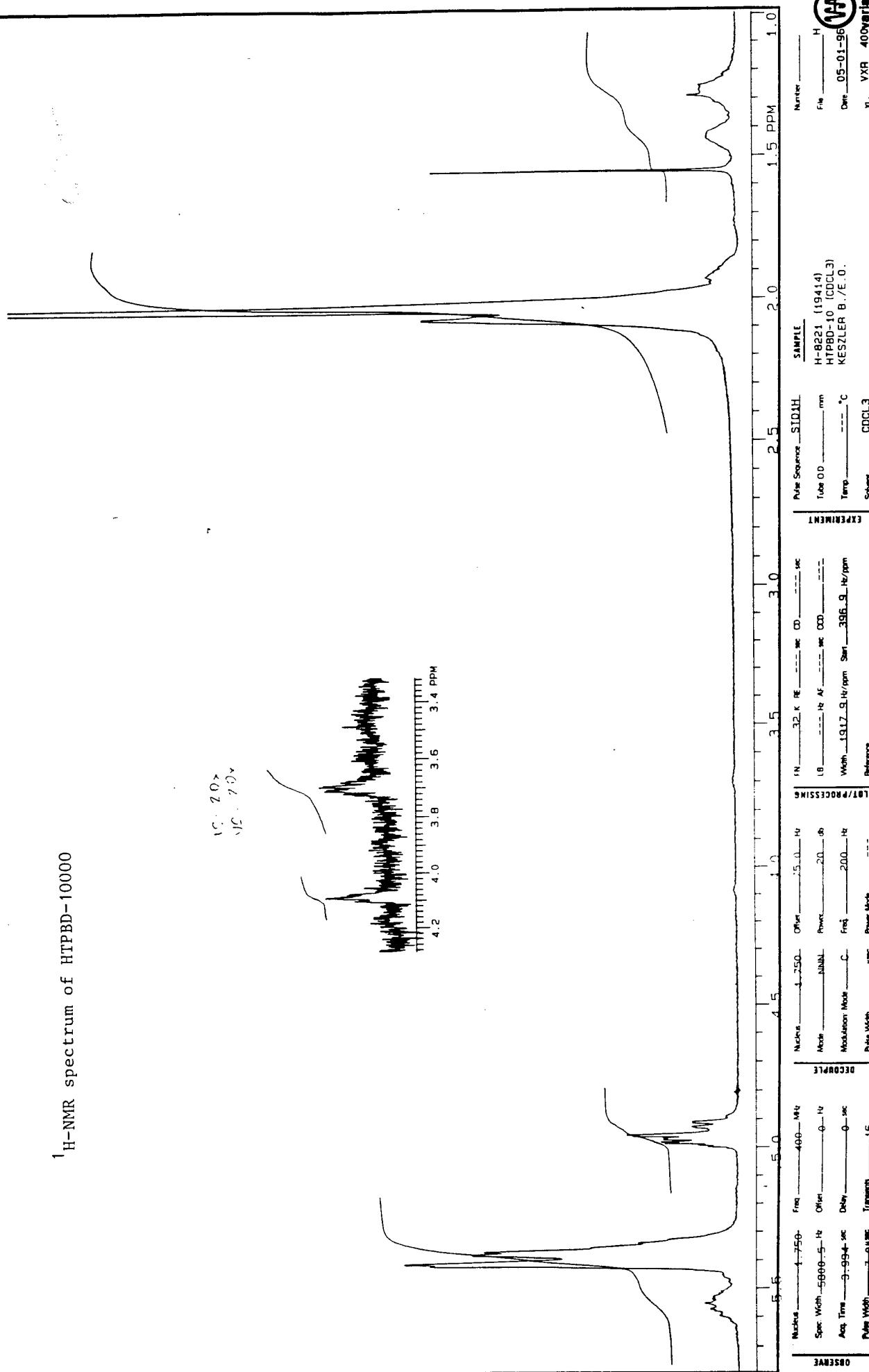




HTPBD — 5000



¹H-NMR spectrum of HTPBD-10000



ANNEX 2

CHARACTERIZATION OF HTPE SAMPLES

- ◆ Molecular weight distribution of precursor HTPBD-1000
- ◆ Molecular weight distribution of precursor HTPBD-1500
- ◆ Molecular weight distribution of precursor HTPBD-2000
- ◆ Molecular weight distribution of precursor HTPBD-3000
- ◆ Molecular weight distribution of precursor HTPBD-5000
- ◆ Molecular weight distribution of precursor HTPBD-10000
- ◆ FT-IR spectrum of precursor HTPBD-1000
- ◆ FT-IR spectrum of precursor HTPBD-1500
- ◆ FT-IR spectrum of precursor HTPBD-2000
- ◆ FT-IR spectrum of precursor HTPBD-3000
- ◆ FT-IR spectrum of precursor HTPBD-5000
- ◆ FT-IR spectrum of precursor HTPBD-10000
- ◆ Proton-NMR spectra of precursor HTPBD-1000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-1500 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-2000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-3000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-5000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-10000 and hydrogenated product

VISCOTEX CORP. UCAL 4.05
FILENAME: 1741a RUN ID: 96/182 Polibut. 174/1a

ENDED: 10/01/96 12:12
Mn = 1.21E3

Mw = 1.87E3

Mz = 3.14E3

MOLECULAR WEIGHT DISTRIBUTION

HTPBD-1000

T-0Tx

(Mw/Mn) M

5.00
4.00
3.00
2.00
1.00

COTEK CORP. UCAL 4.05
ENAME: 174k2 RUN ID: 96/184 Poli but. 174/k2

ENDED: 10/01/96 13:26

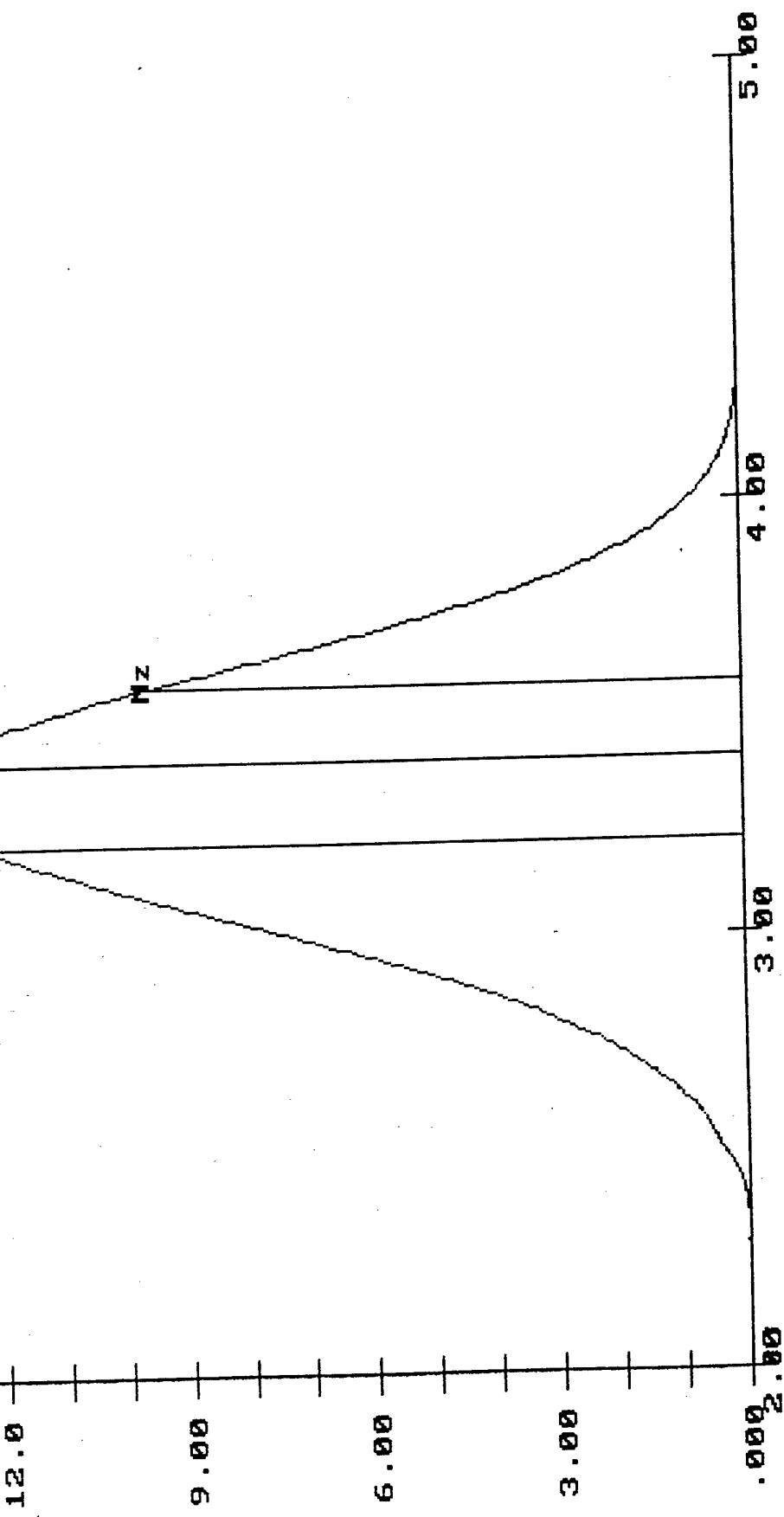
$M_n = 1.67 \times 10^3$

$M_w = 2.55 \times 10^3$

$M_z = 3.81 \times 10^3$

MOLECULAR WEIGHT DISTRIBUTION

HTPB0 - 1500



ENDED : 09/24/96 12:01

UCAL 4.05

VISCOTEM CORP.

FILENAME: 161K RUN ID: 96/175 Polibut. 161/k

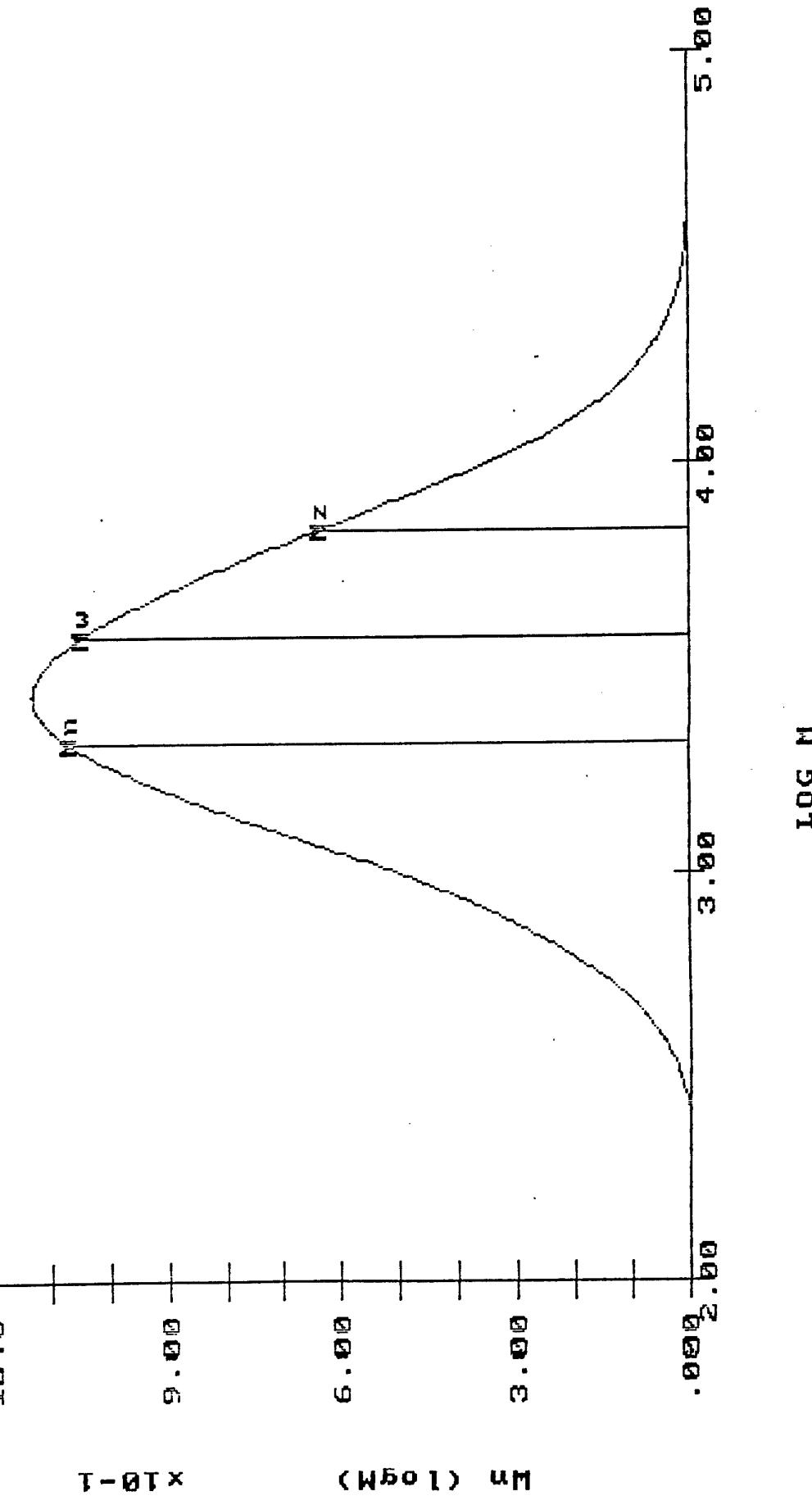
Mn = 2.14E3

Mw = 3.83E3

Mz = 6.92E3

MOLECULAR WEIGHT DISTRIBUTION

HTPBD 2000

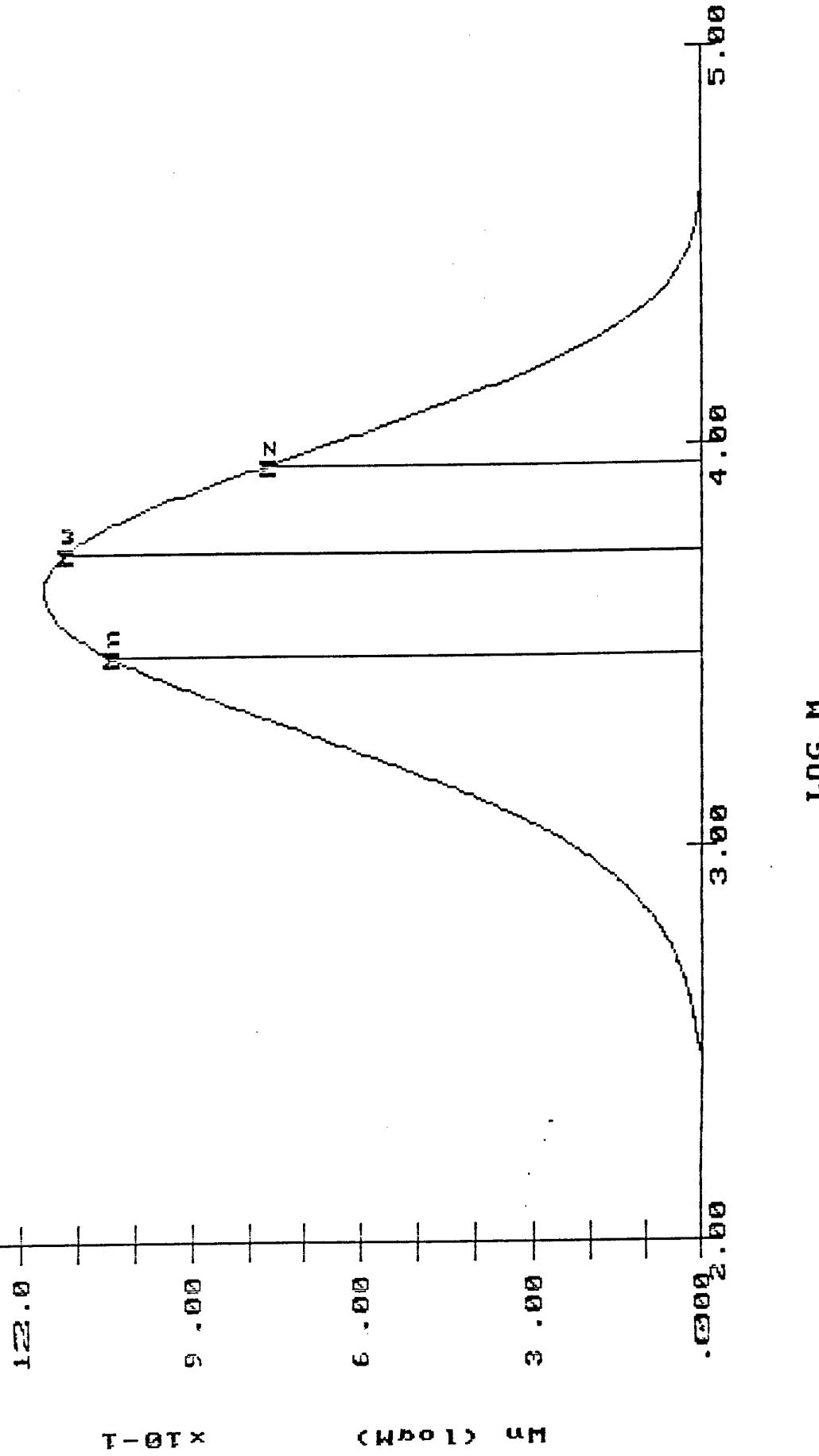


VISCO-TEK CORP. UCAL 4.05
FILENOME: 154160 RUN ID: 96/143 Polibut. 154,160 min a

END: 08/13/96 13:45
Mn = 3.06E3 Mw = 5.44E3
Mz = 9.06E3

MOLECULAR WEIGHT DISTRIBUTION

HTPBD 3000



DISCUTER CURP.

FILENAME: 1751 RUN ID: 96/185 Pollibut. 175/1

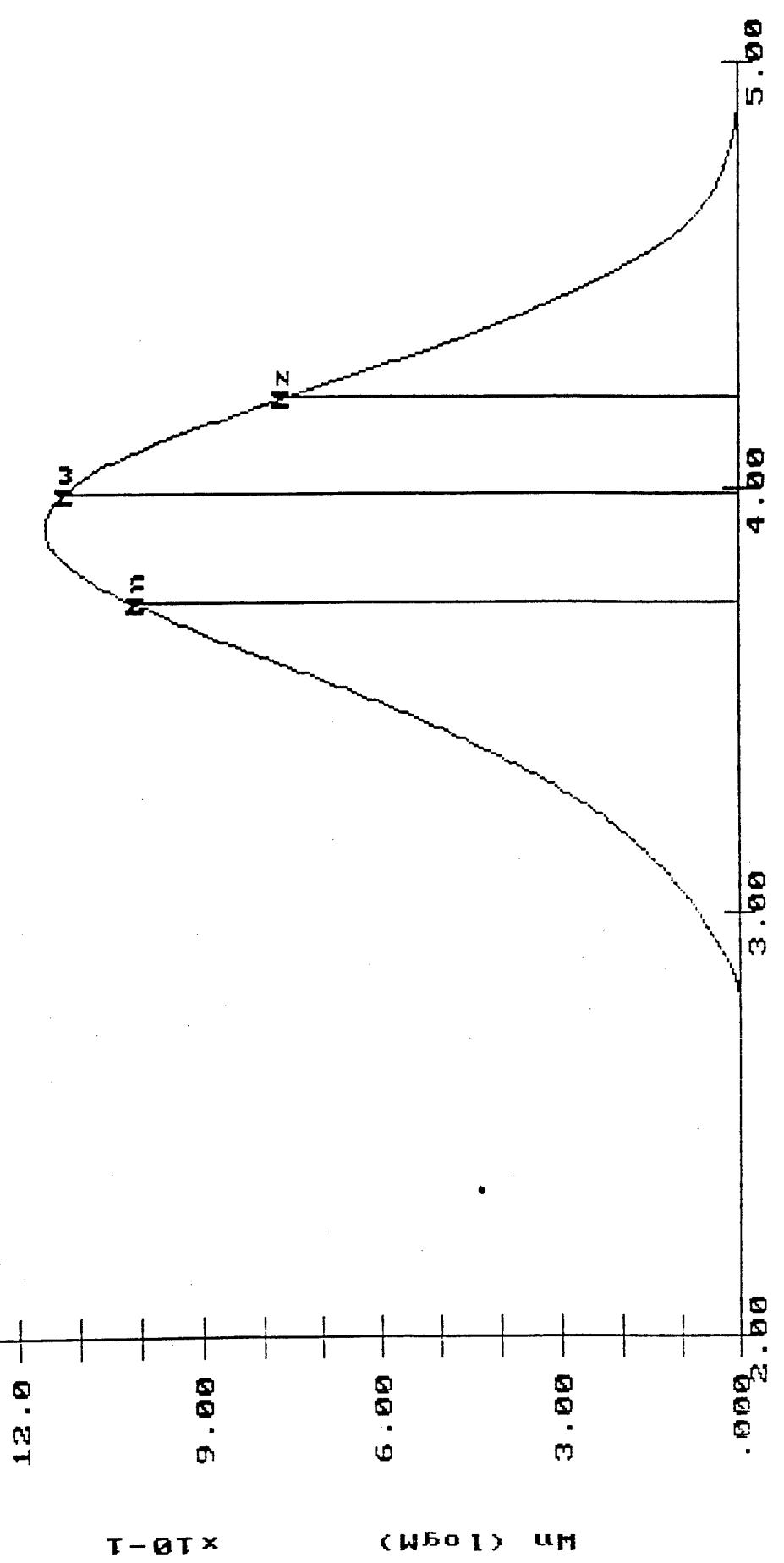
$M_n = 5.40 \times 10^3$

$M_w = 9.76 \times 10^3$

$M_z = 1.63 \times 10^4$

MOLECULAR WEIGHT DISTRIBUTION

HTPBD-5000



VISCO-TEX CORP.

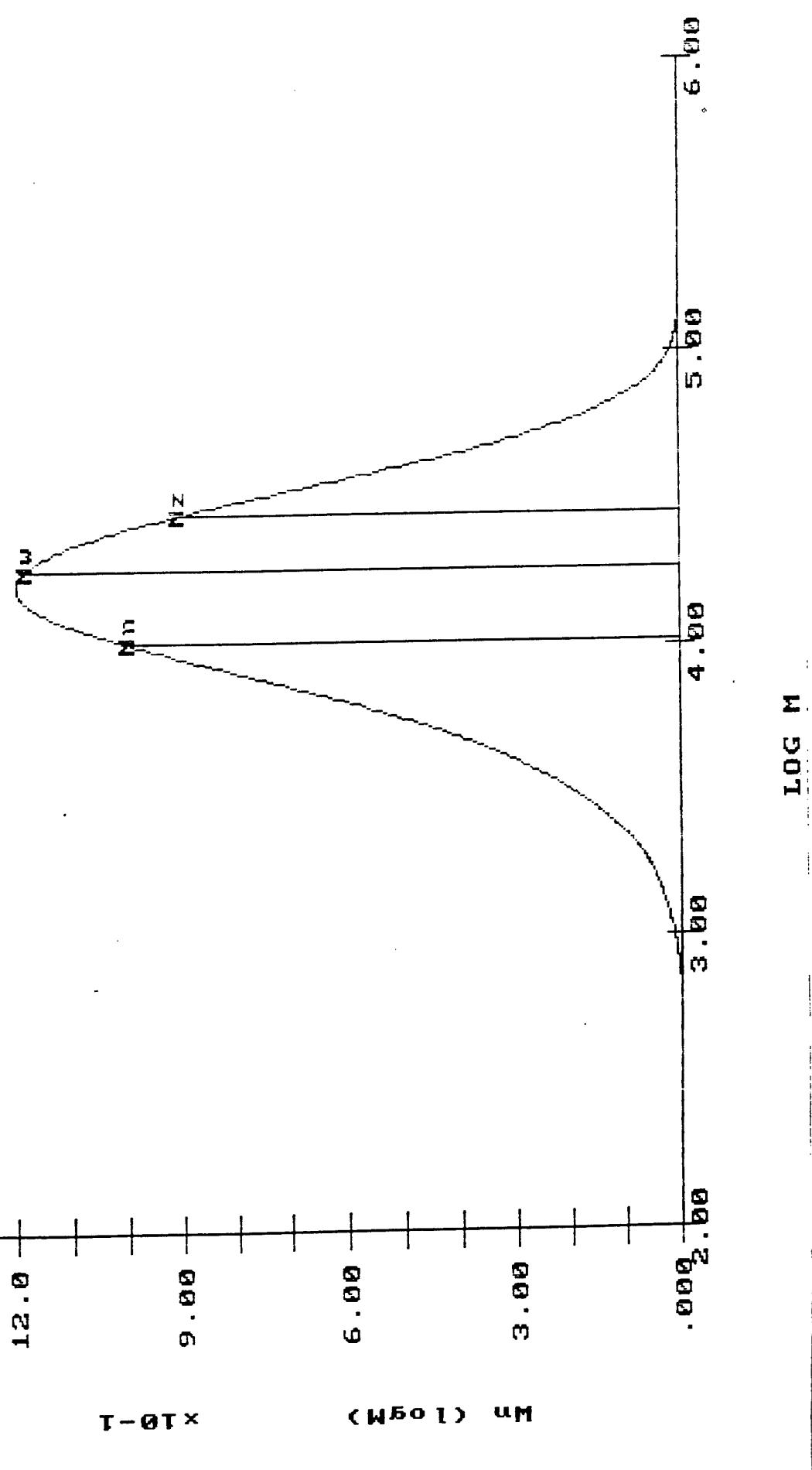
FILE NAME: 167fob UCAL 4.05 ENDED: 09/09/96 12:55

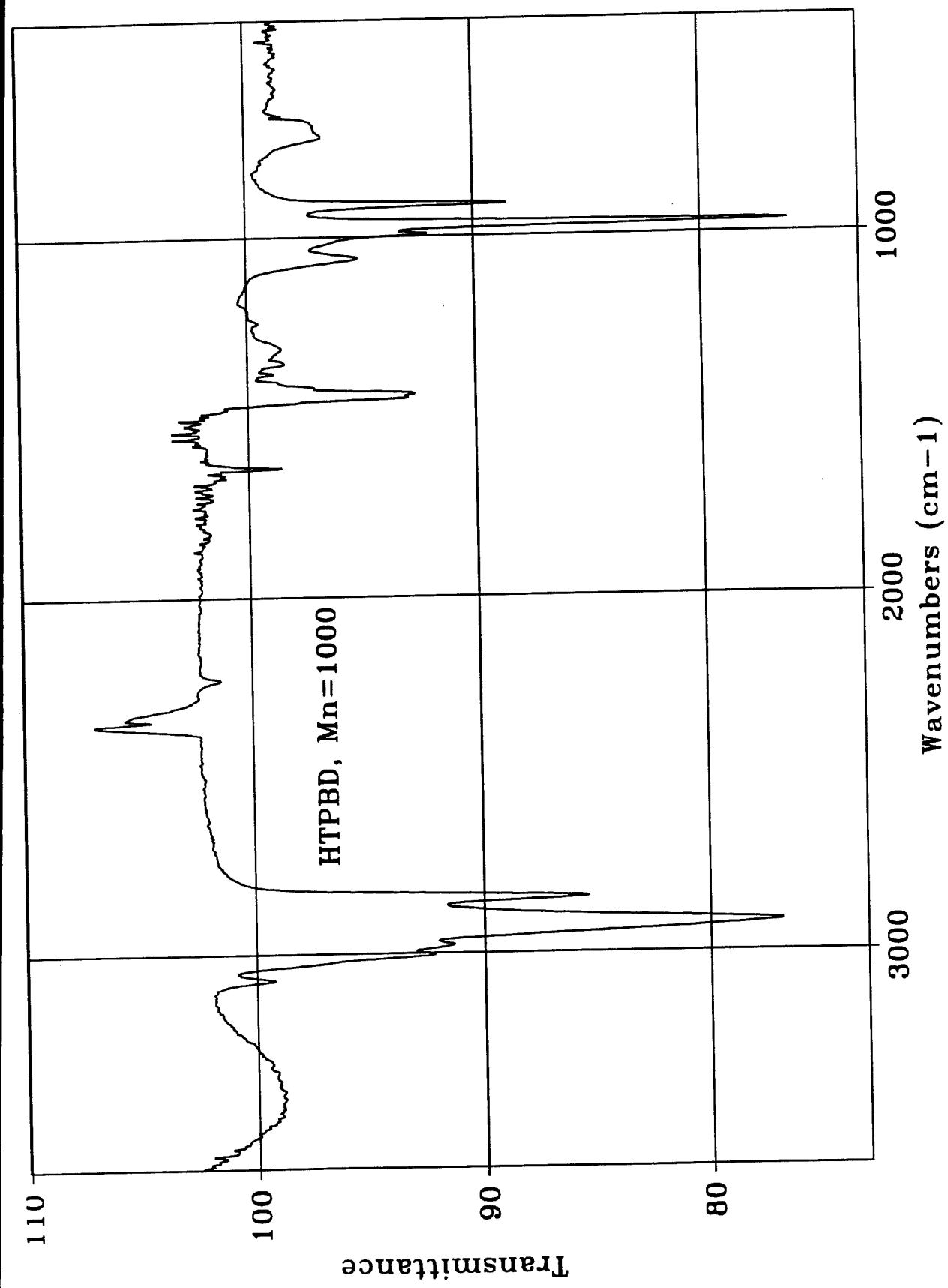
RUN ID: 96/158 Polibut. 167/fob Mn = 1.03E4

M_w = 1.33E4 MOLECULAR WEIGHT DISTRIBUTION

M_z = 2.86E4

HTPBD - 10000





Transmittance

HTPBD, Mn=1000

3000

2000

1000

Wavenumbers (cm⁻¹)

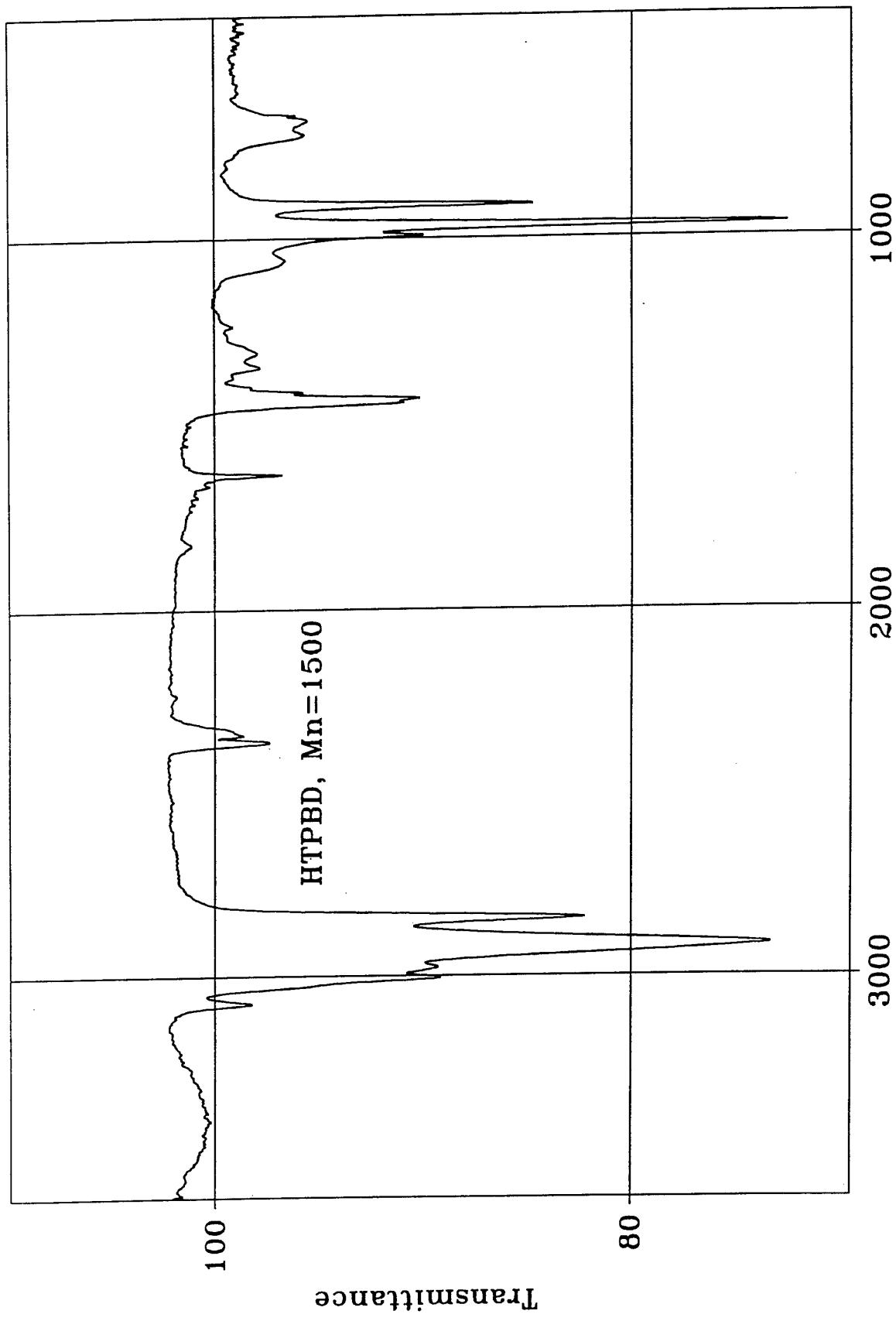
100

90

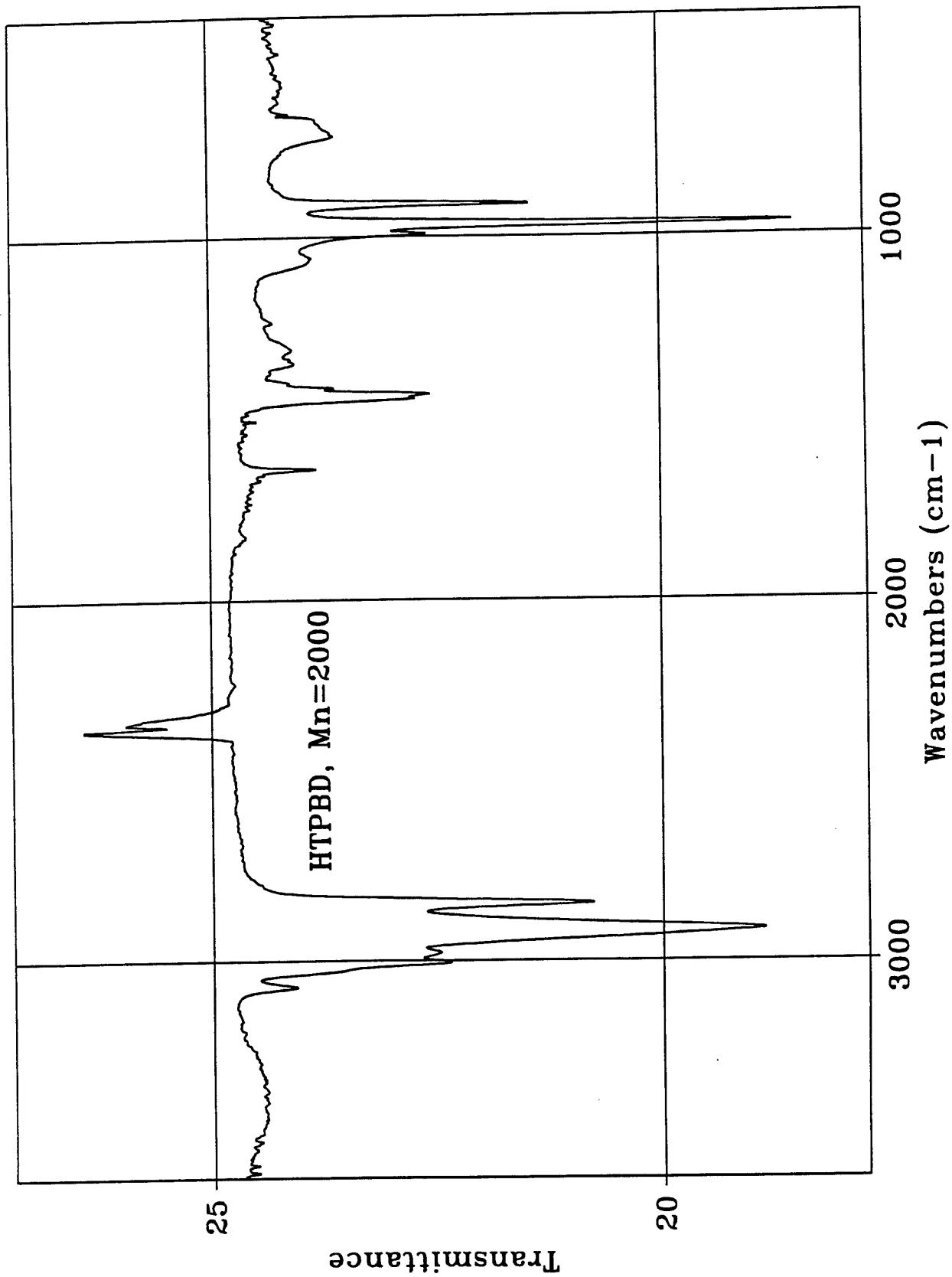
80

Res= 4 cm⁻¹

01/29/97 02:28



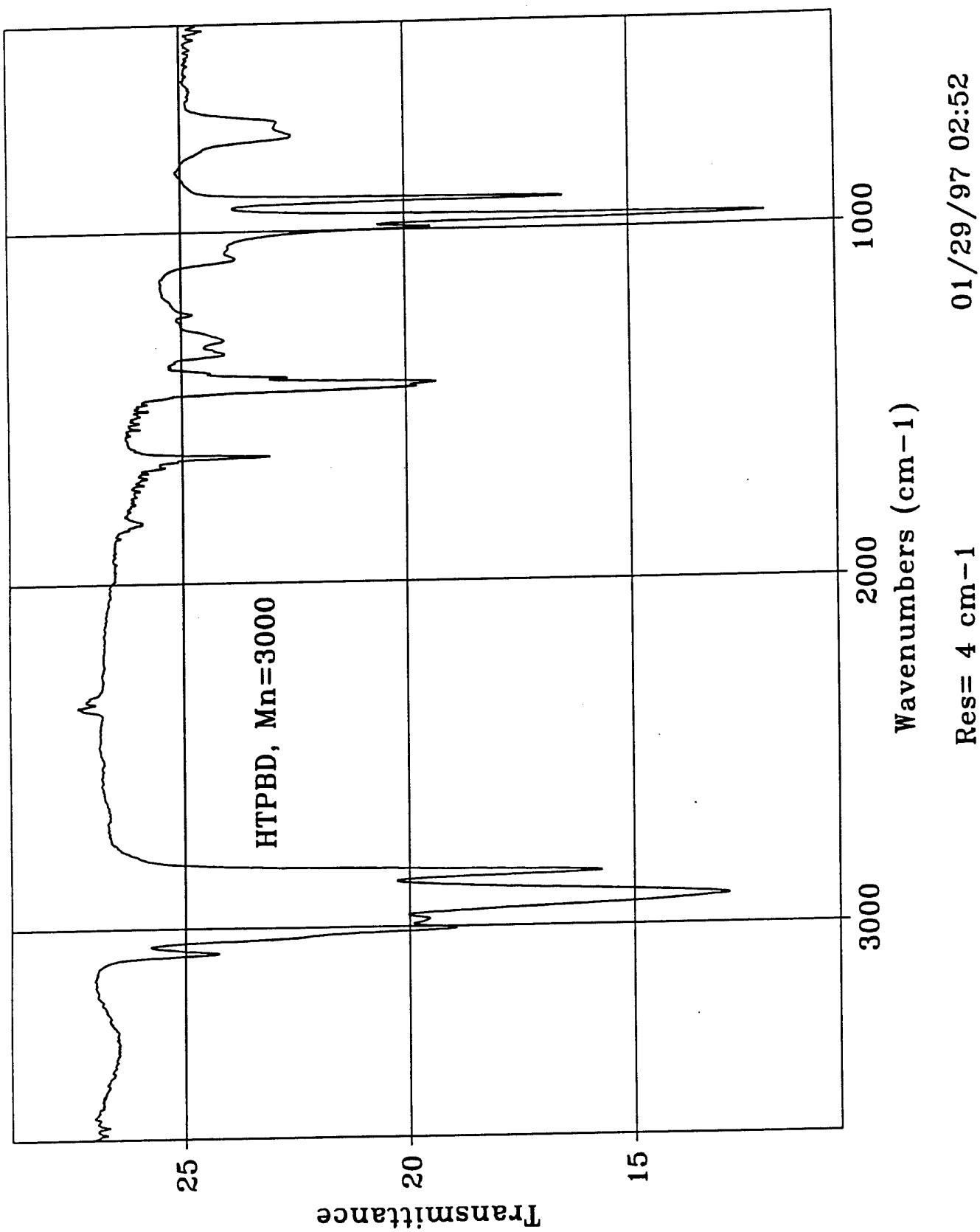
01/29/97 02:37

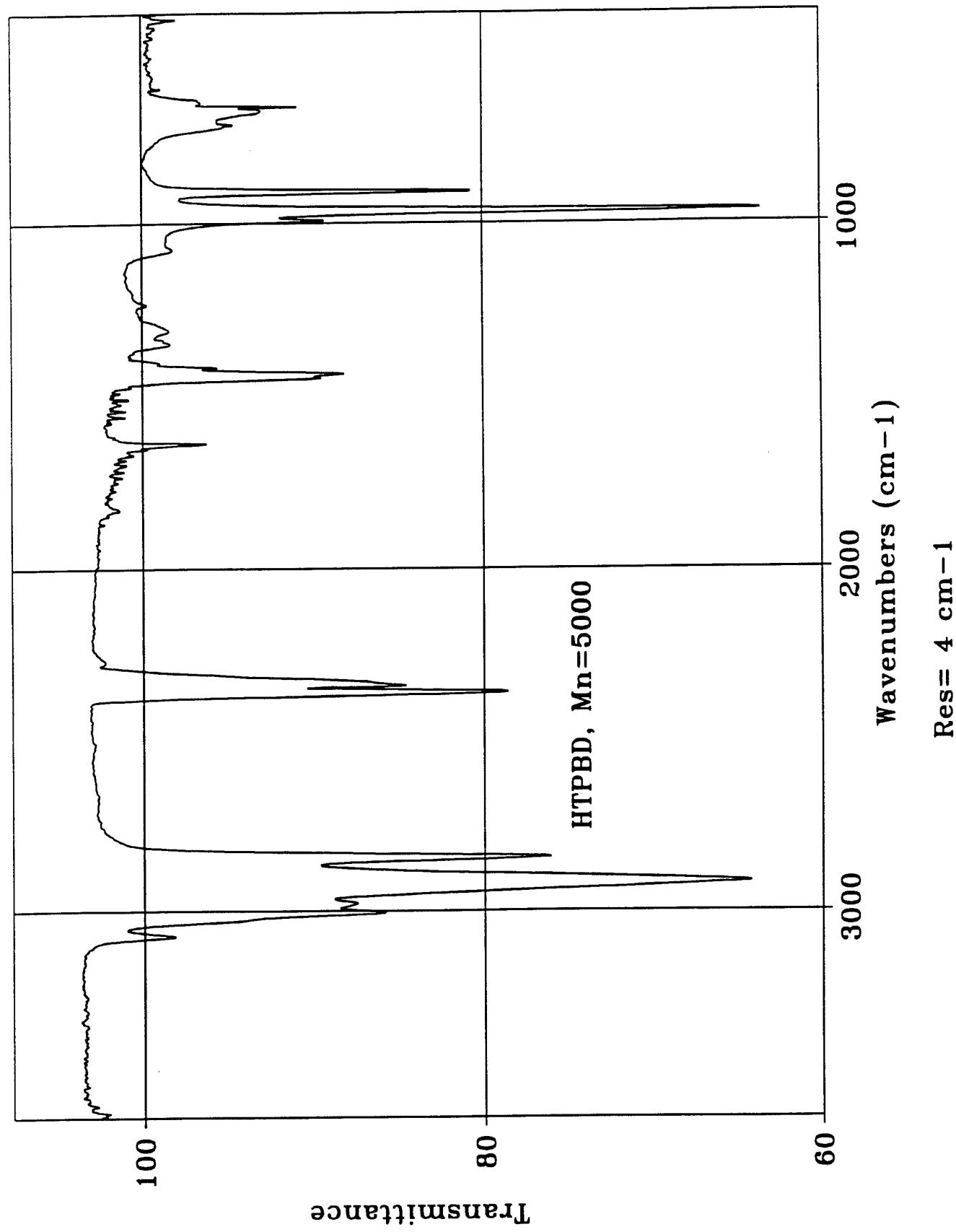


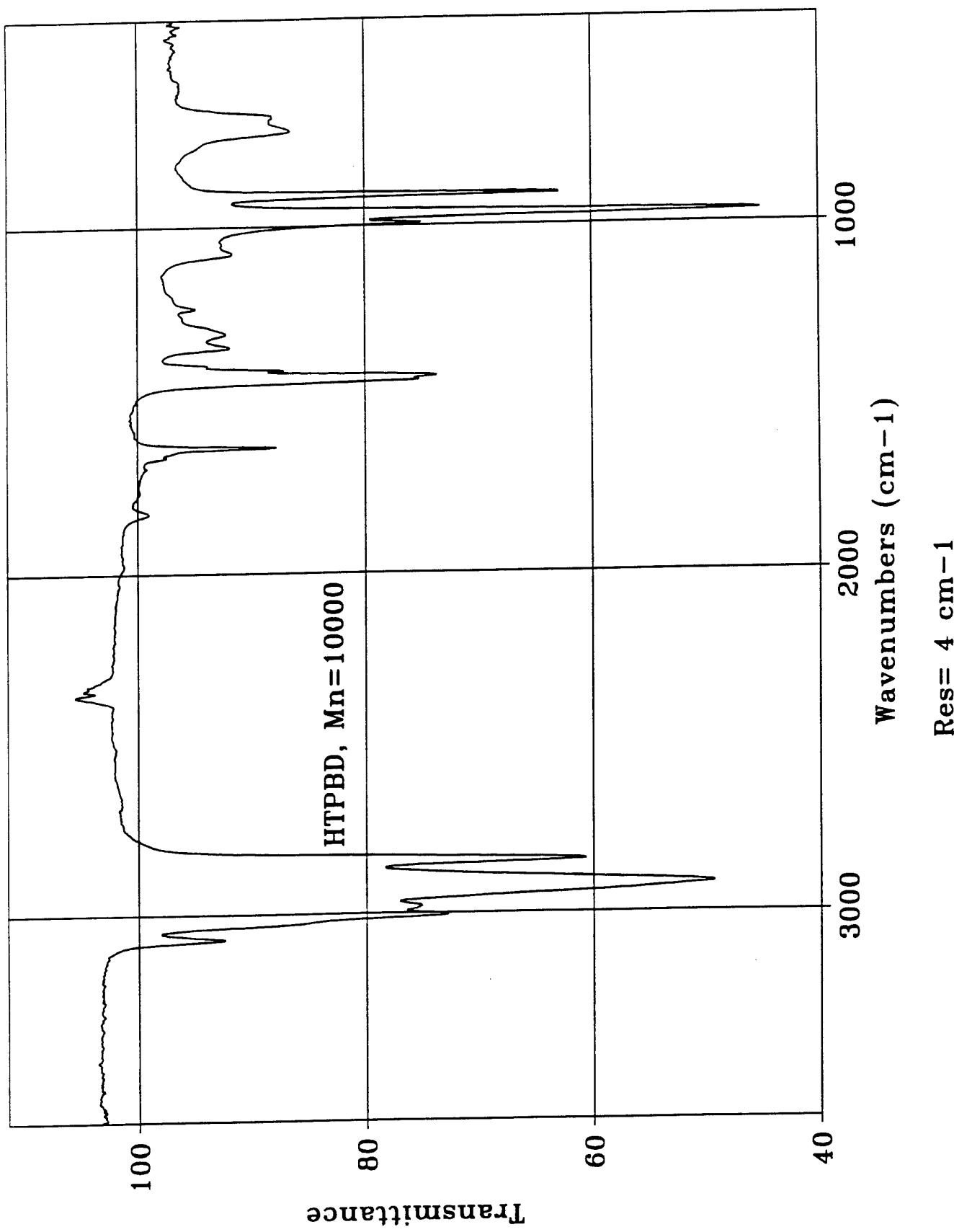
01/29/97 02:45

Res= 4 cm⁻¹

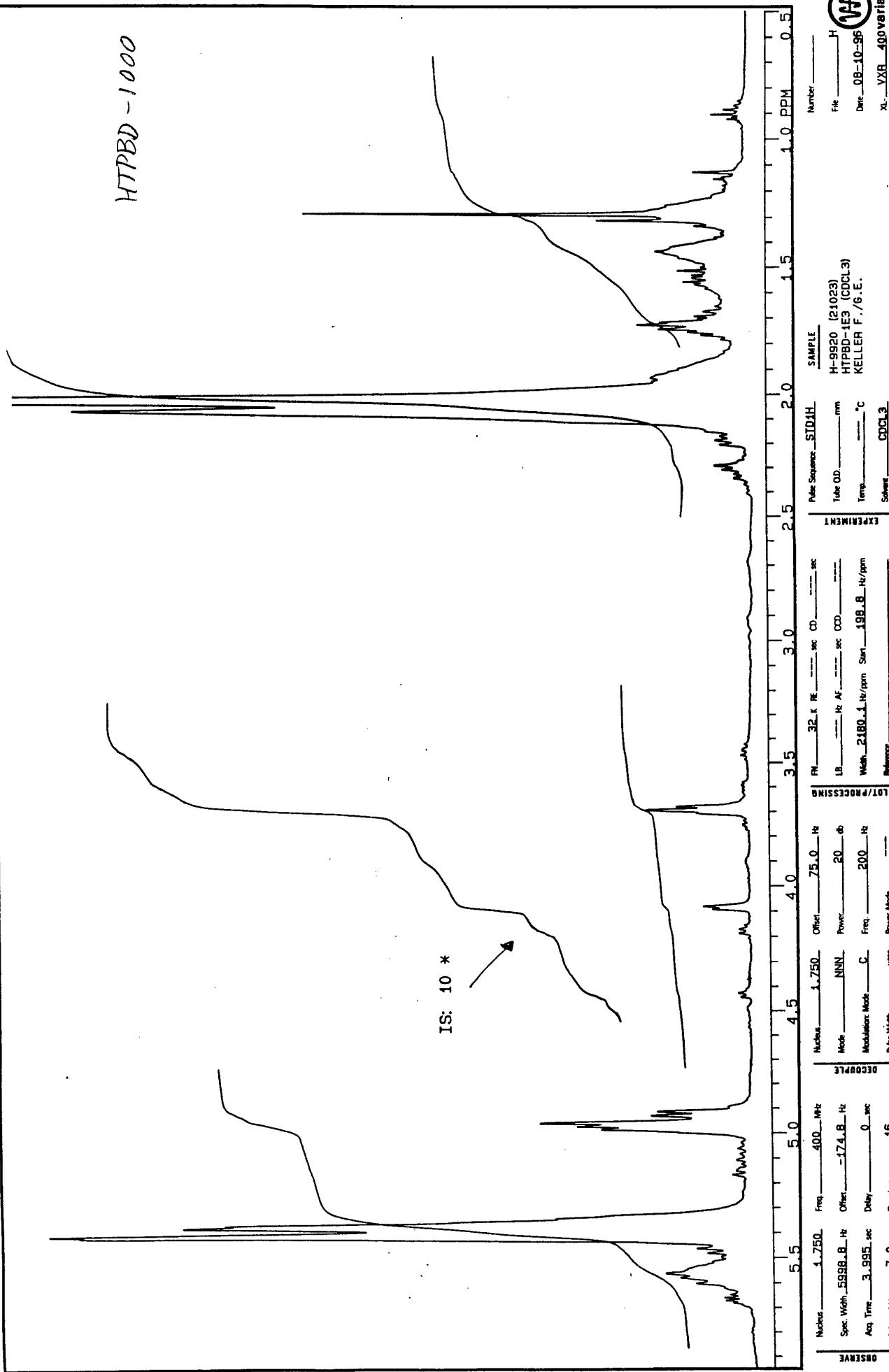
Wavenumbers (cm⁻¹)





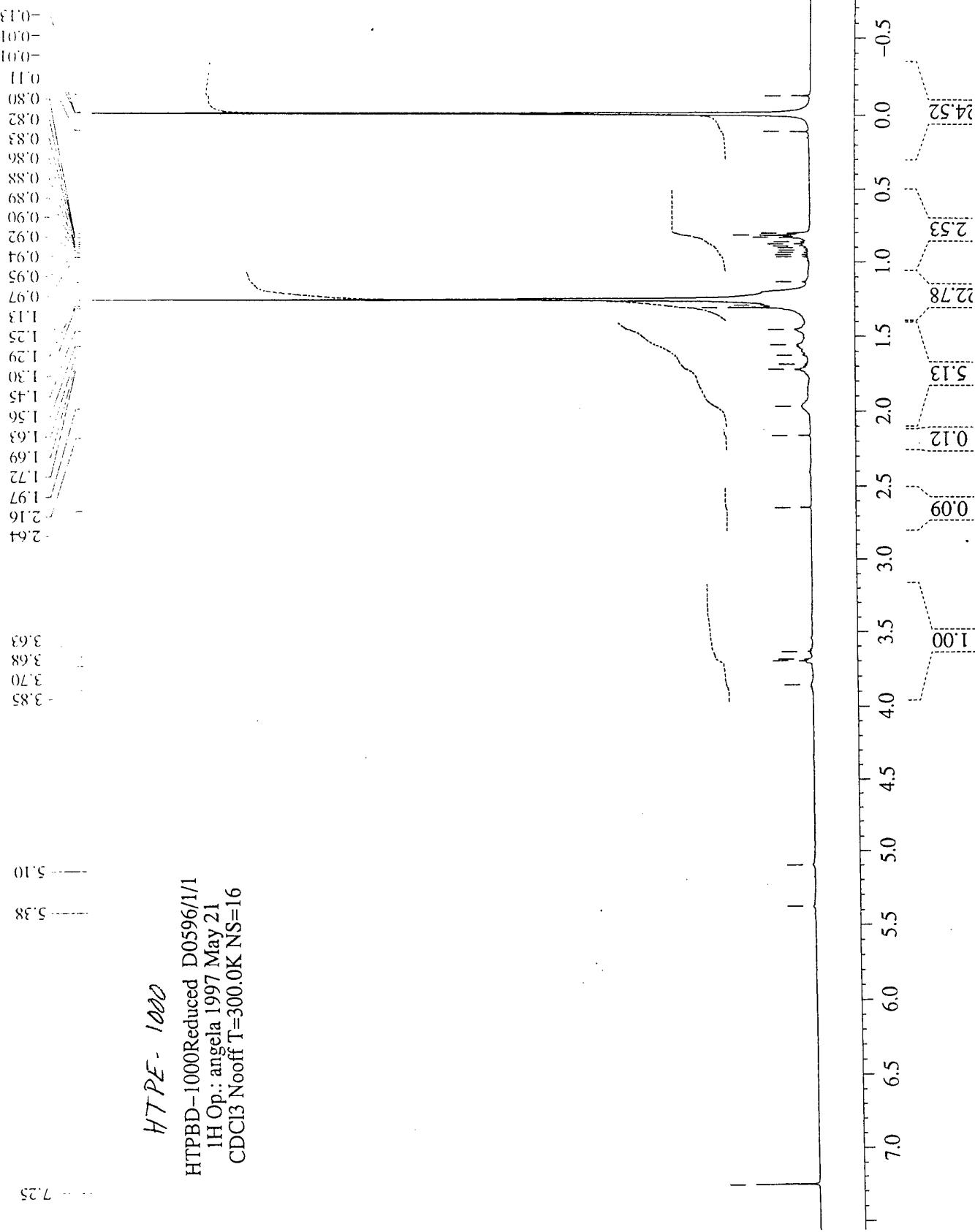


HTPBD - 1000

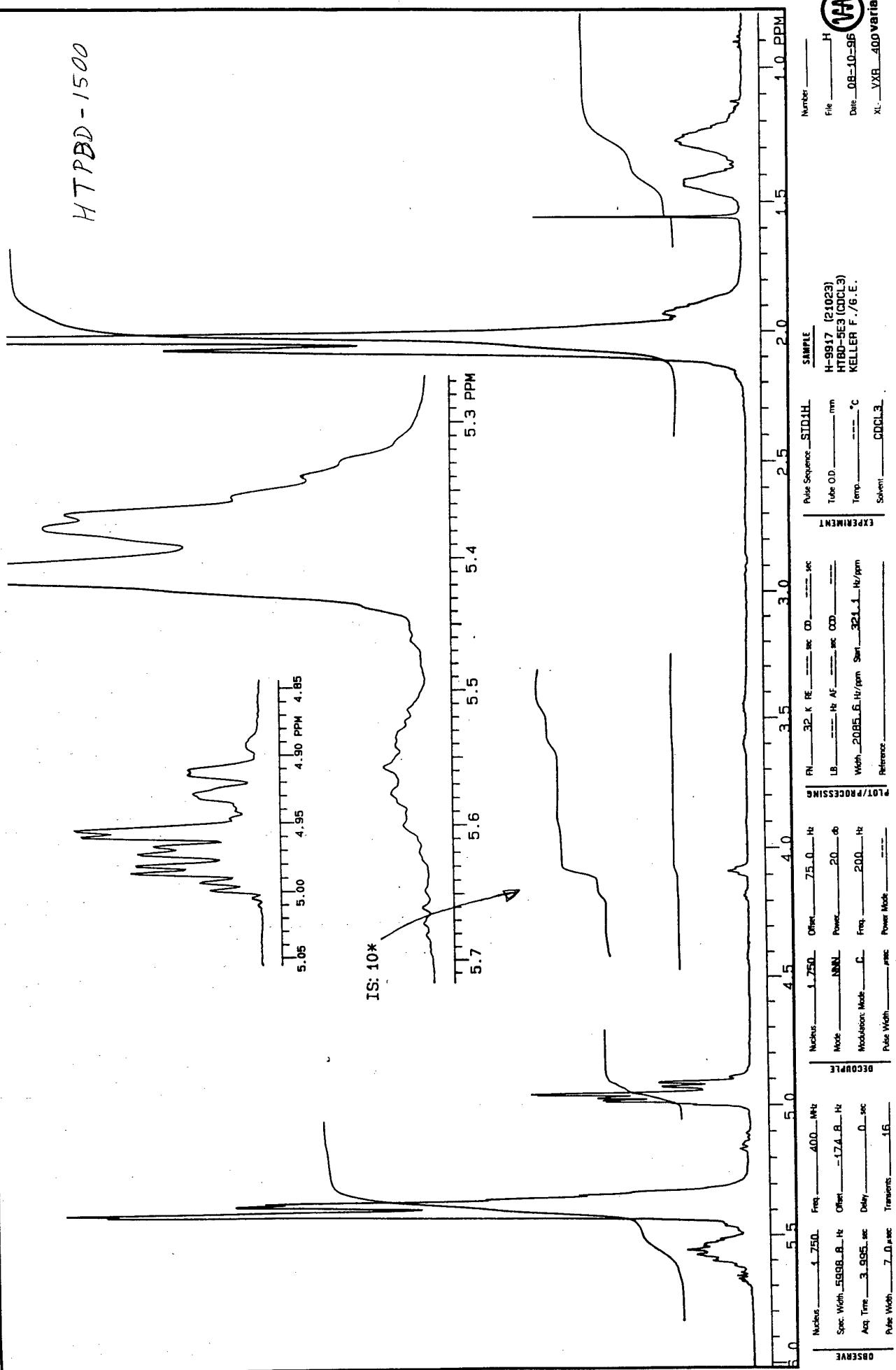


HTPE-1000

HTPBD-1000 Reduced D0596/1/1
1H Op.: angela 1997 May 21
CDCl₃ Noff T=300.0K NS=16

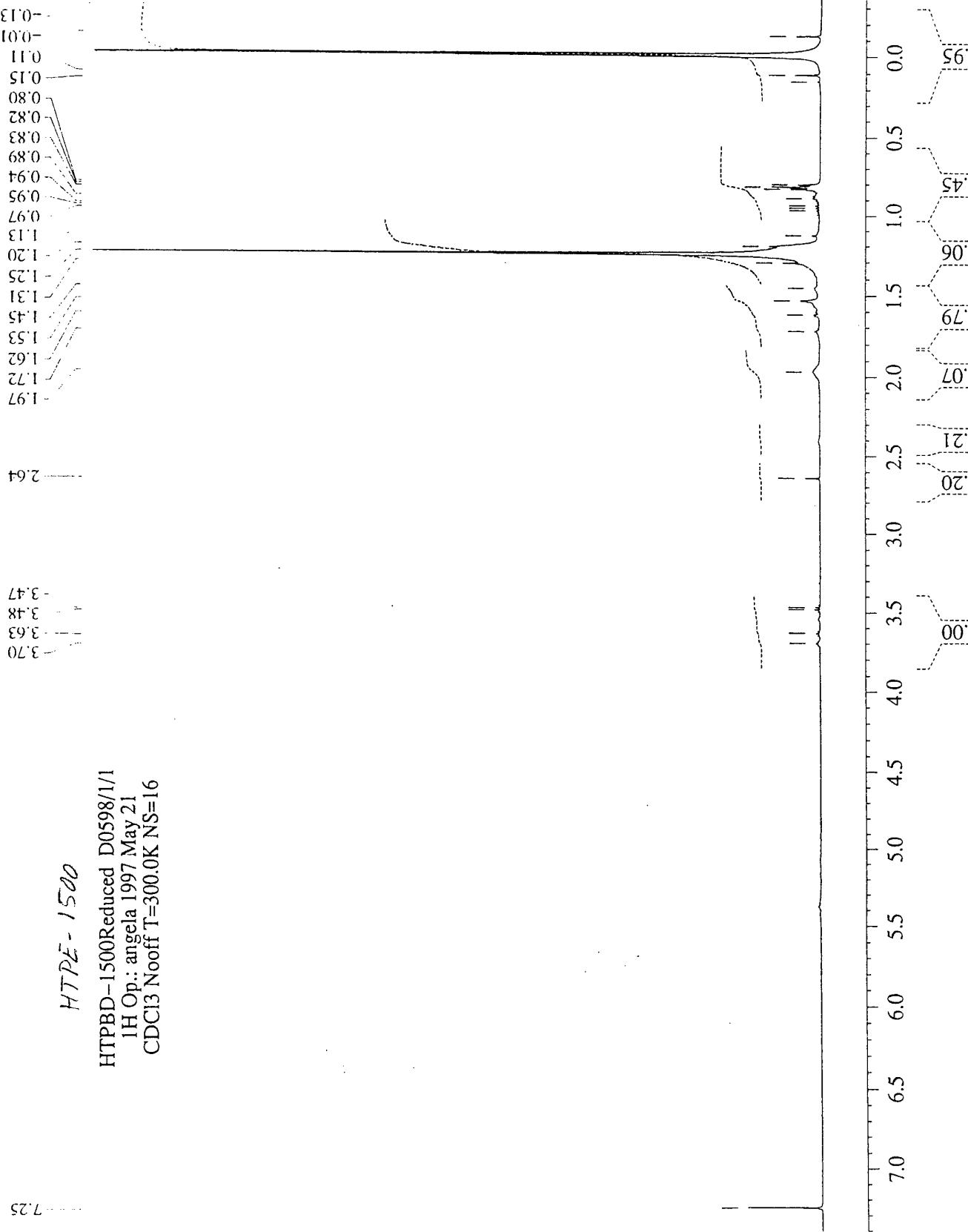


HTPBD-1500

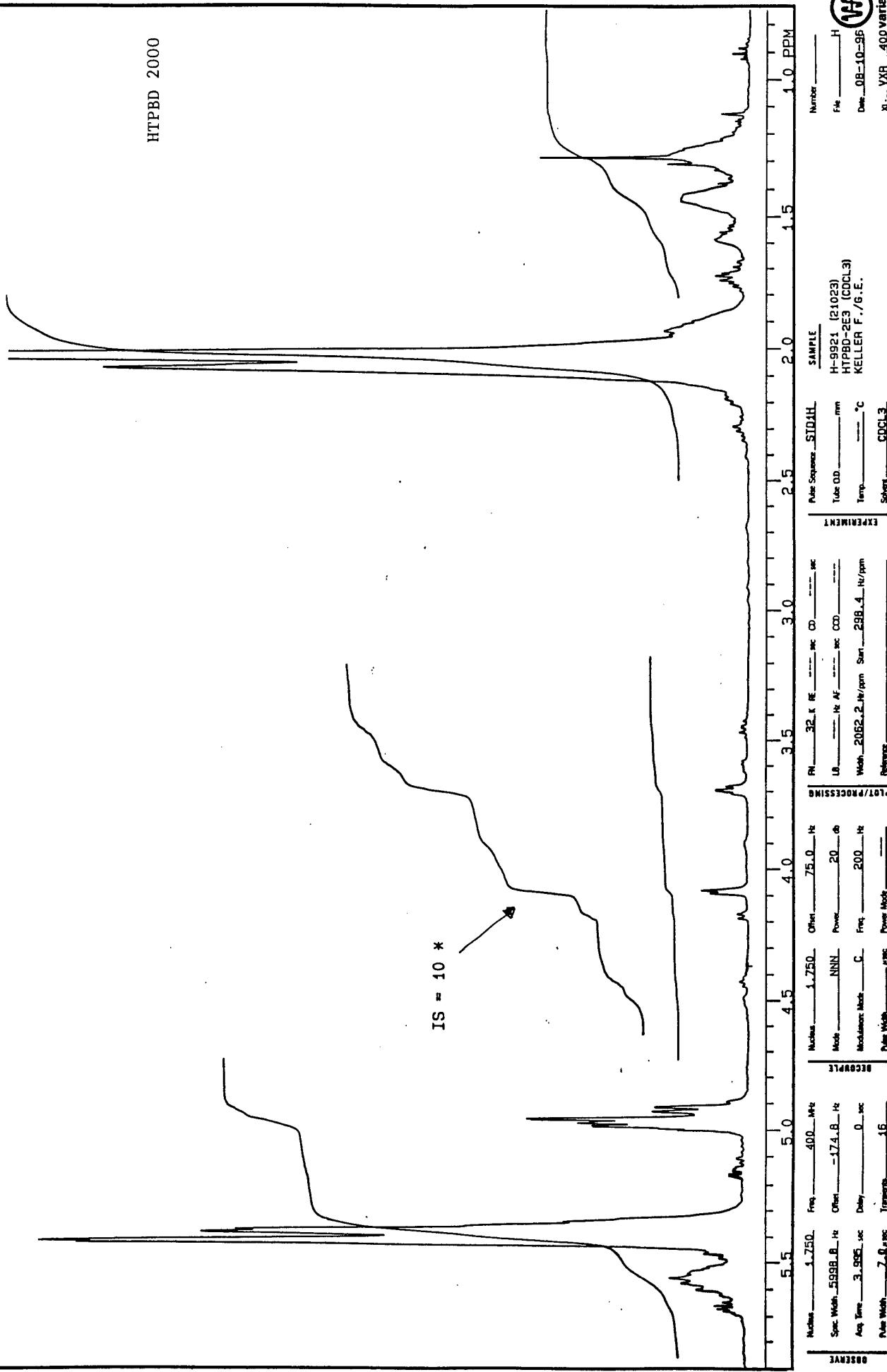


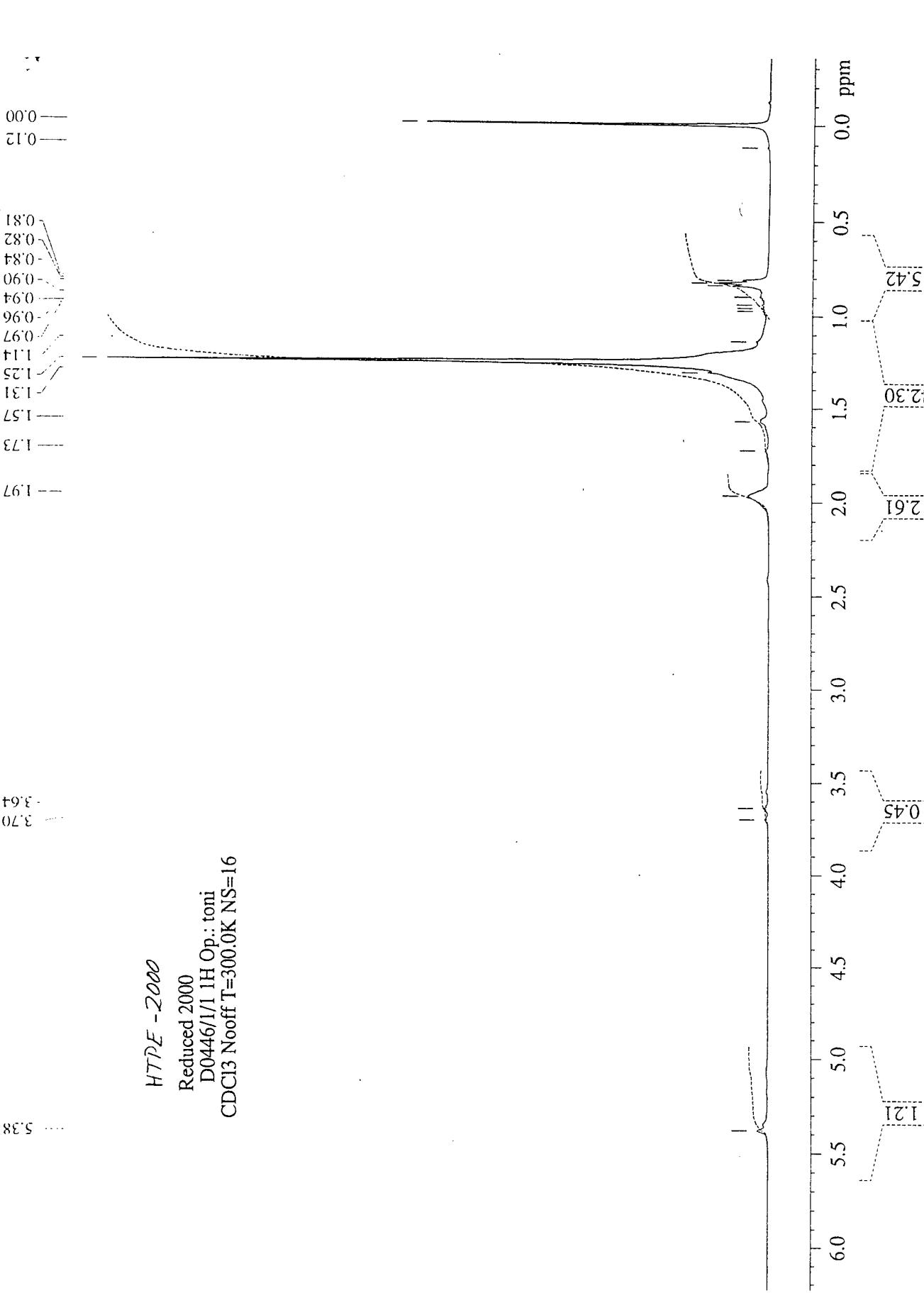
HTPBD-1500

HTPBD-1500 Reduced D0598/1/1
1H Op.: angela 1997 May 21
CDCl₃ Noff T=300.0K NS=16

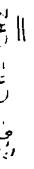
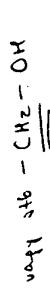
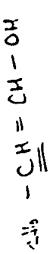
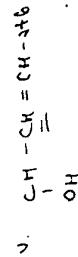
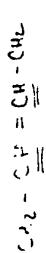


HTPBD 2000

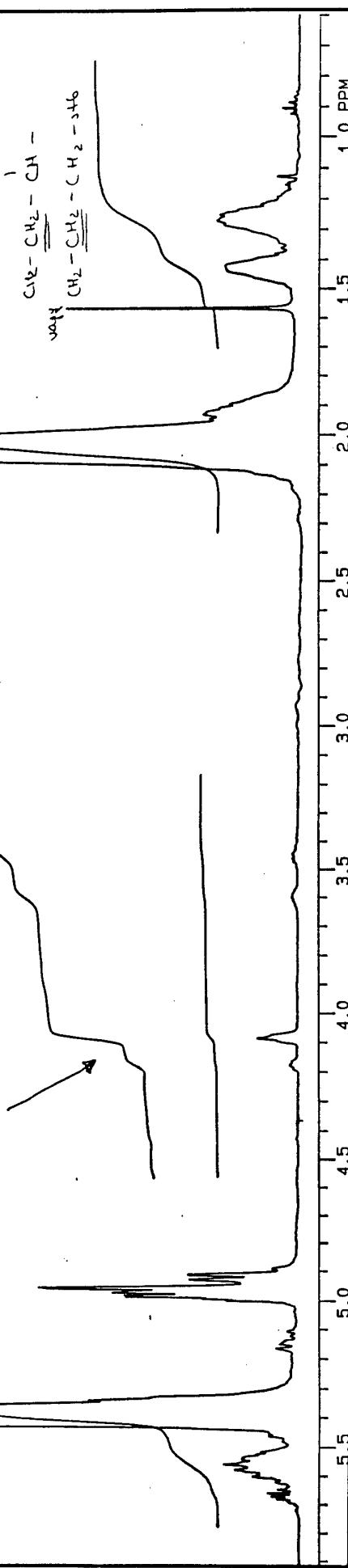




HTPBD 3000



IS = 10 *



SAMPLE		Pulse Sequence: SIDAK		Pulse Sequence: SIDAK	
File	KE3E3	File	KE3E3	File	KE3E3
H-9322	(21023)	H-9322	(21023)	H-9322	(21023)
HTPBD-3E3	(CDCl3)	HTPBD-3E3	(CDCl3)	HTPBD-3E3	(CDCl3)
KELLER / G.E.		KELLER / G.E.		KELLER / G.E.	
Date 08-10-96		Date 08-10-96		Date 08-10-96	
XN...VXB_400 varian		XN...VXB_400 varian		XN...VXB_400 varian	
Spec. Width	50.0 Hz	Spec. Width	50.0 Hz	Spec. Width	50.0 Hz
Freq.	400.0 MHz	Freq.	32.0 MHz	Freq.	32.0 MHz
Offset	-174.8 Hz	Offset	-75.0 Hz	Offset	-75.0 Hz
Power	20.0	Power	20.0	Power	20.0
Mode	NNN	Mode	NNN	Mode	NNN
31400338		31400338		31400338	
Modulation Mode	0.0 sec	Modulation Mode	0.0 sec	Modulation Mode	0.0 sec
Delay	0.0 sec	Delay	0.0 sec	Delay	0.0 sec
Freq.	2426.7 Hz/psm	Freq.	200.0 Hz	Freq.	239.8 Hz/psm
Time		Time		Time	
Transients	16	Transients	16	Transients	16
Pulse Width	7.0, 1.0 sec	Pulse Width	7.0, 1.0 sec	Pulse Width	7.0, 1.0 sec
Reference					

File: KE3E3
 Date: 08-10-96
 XN...VXB_400 varian
 Number: 1
 File: KE3E3
 Date: 08-10-96
 XN...VXB_400 varian
 Number: 2
 File: KE3E3
 Date: 08-10-96
 XN...VXB_400 varian
 Number: 3

-0.01
0.00
0.01

-0.81
-0.82
-0.84
-1.25

0.01
0.00
0.01

1.00

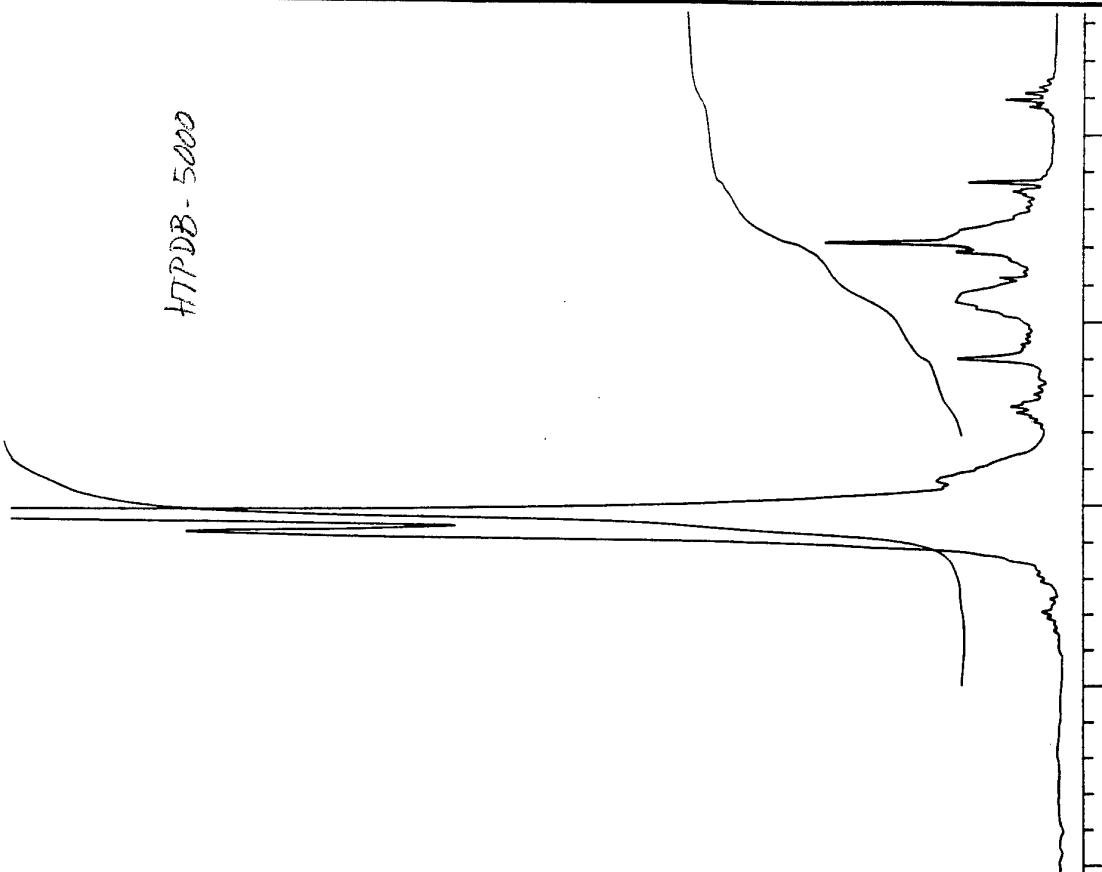
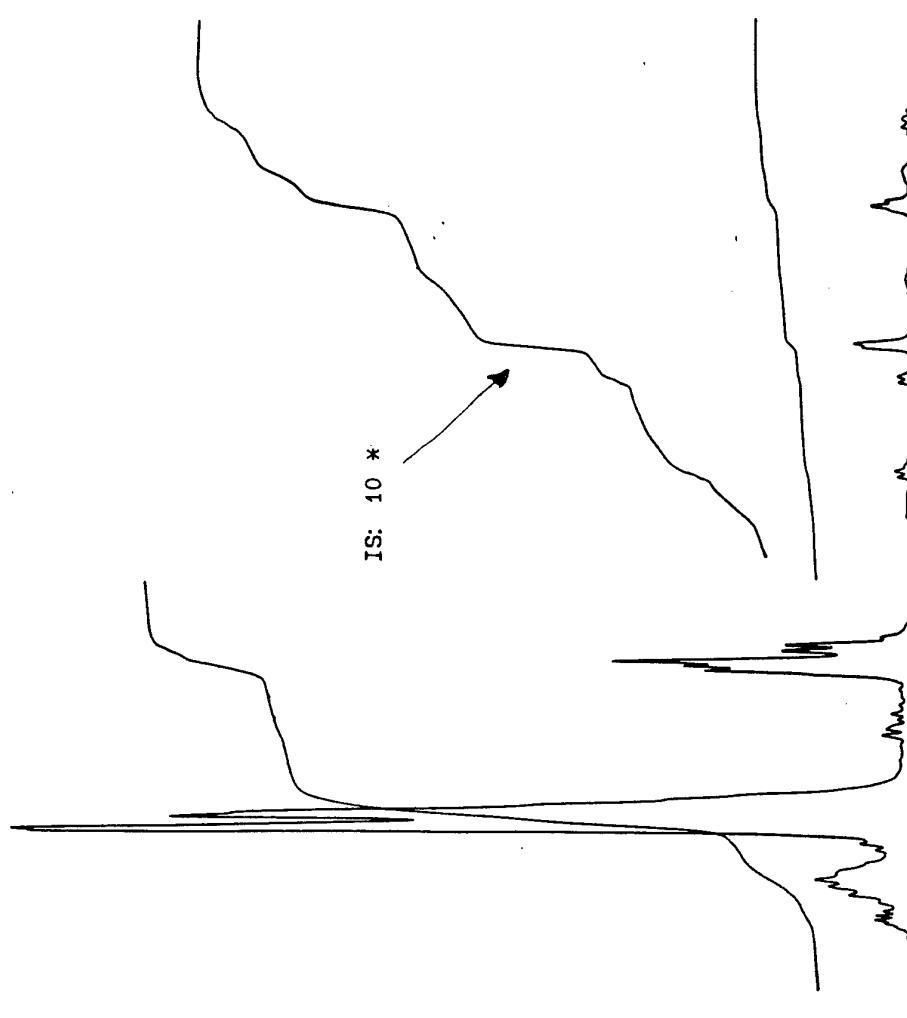
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0

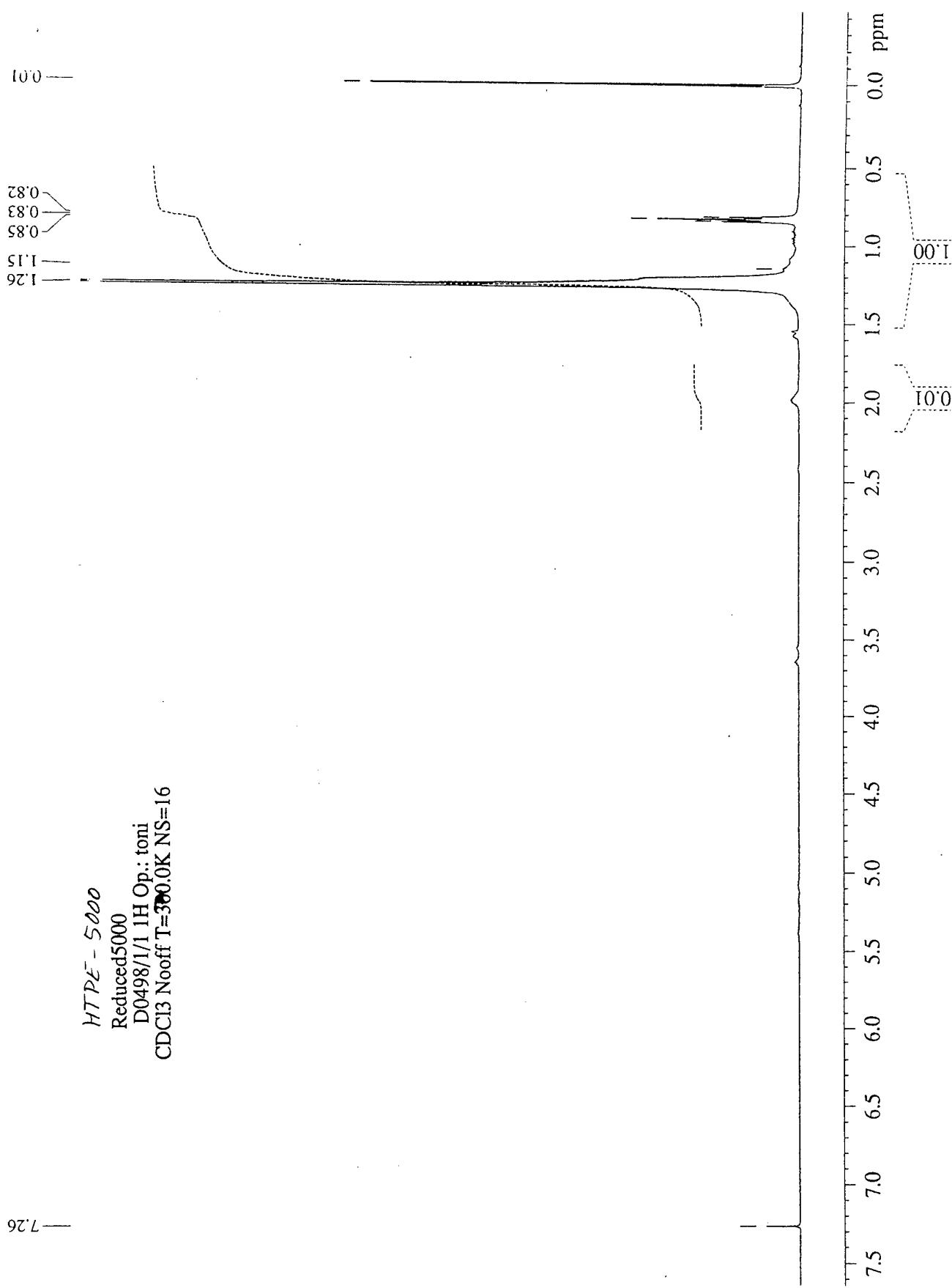
H *T* *P* *E* - 3000
REDUCED3000
D0479/1/1 1H Op.: angela
CDC13 Noff T=300.0K NS=16

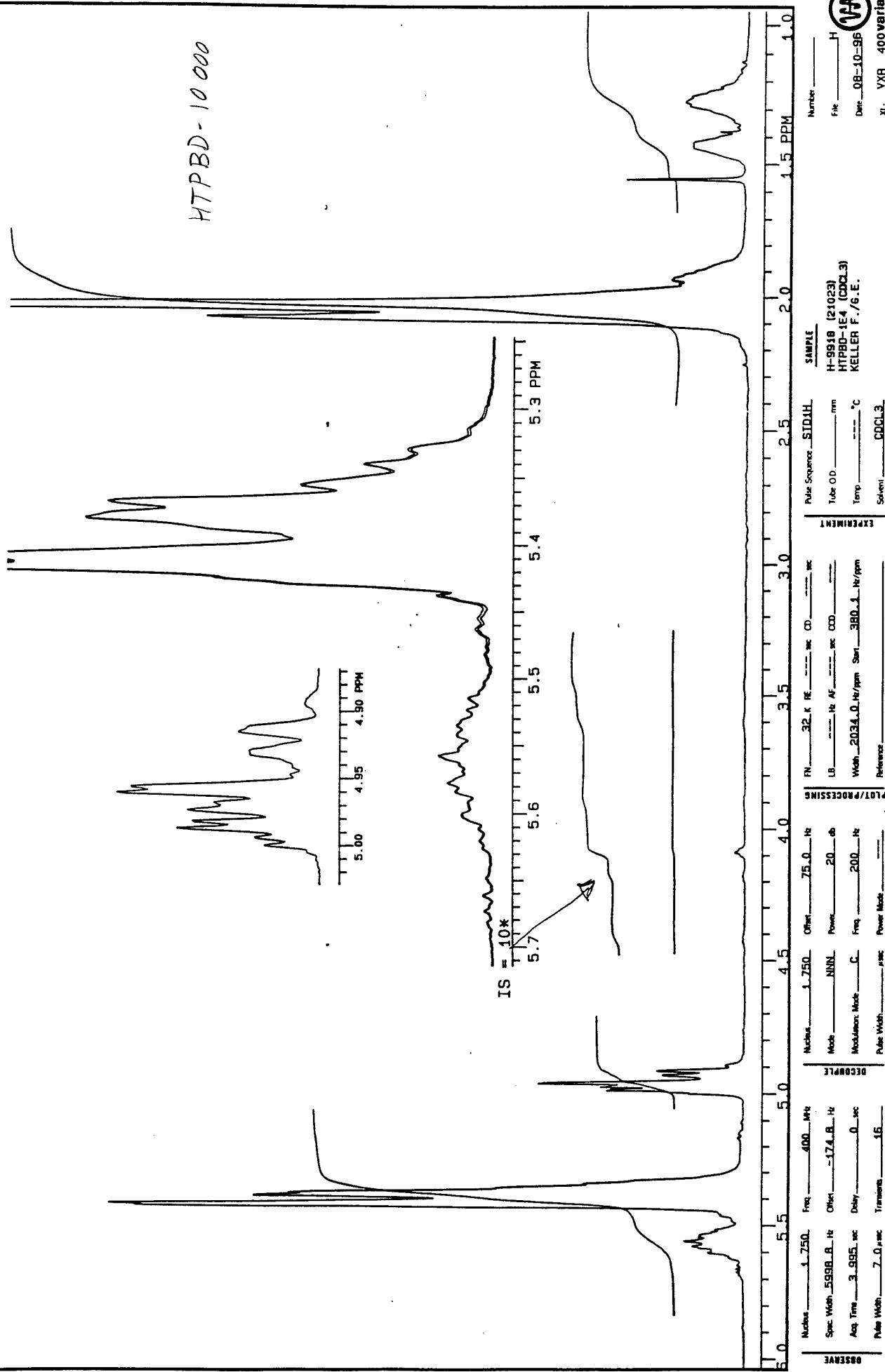
7.26

HTTDB - 5000



Spec. Wtch -5956-0 Hz Offset -747-0 Hz Mode -NNNN- Power -20-0
 Acc. Tim -3.995- sec Delay -0- sec Modulation Mode -C- Freq -200- Hz
 Rate Wtch -7-0- sec Transients -16- Pulse Width -1.0- sec Power Mode -
 PLATE/PROCESSED BY 33488530 EXPERIMENT H-9949-121023
 File _____ H _____ Date DB-10-96
 XL - VAB - 400 varian
 HTPBD-1, 5E3 (COL3)
 KELLER F. /G. E.
 Tube OD _____ mm
 Temp _____ °C
 Scheme - COL3
 Reference -
 Watch -2432.5 Hz/ rpm Scan -269.9 Hz/ rpm





HTPE-10.000
Reduced 10000
D0496/1/1 1H Op.: toni
CDCl₃ N6off T=300.0K NS=32

0.00
-0.01

1.53
1.25
1.21
0.84
0.82
0.81

1.00
2.28
0.115
1.00
2.28

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 ppm

7.26